ACTA UNIVERSITATIS SZEGEDIENSIS

# ACTA MINERALOGICA-PETROGRAPHICA

## FIELD GUIDE SERIES

Volume 7 Szeged, 2010

VOJTĚCH ETTLER, JIŘÍ SEJKORA, PETR DRAHOTA, JIŘÍ LITOCHLEB, PETR PAULIŠ, JOSEF ZEMAN, MILAN NOVÁK & JAN PAŠAVA

**Příbram and Kutná Hora mining districts – from historical mining to recent environmental impact**

**IMA2010 FIELD TRIP GUIDE CZ3**



*Published by the Department of Mineralogy, Geochemistry and Petrology, University of Szeged*

# ACTA MINERALOGICA-PETROGRAPHICA
*estabilished in 1923*

## FIELD GUIDE SERIES

HU ISSN 0324-6523
HU ISSN 2061-9766





**Guest Editor of this Volume**
Gábor Papp
*Hungarian Natural History Museum, Budapest, Hungary*
*E-mail: pappmin@ludens.elte.hu*



This volume was published for the 375th anniversary of the Eötvös Loránd University, Budapest.

The publication was co-sponsored by the Eötvös University Press Ltd., Budapest.

IMA2010 (www.ima2010.hu) is organised in the frame of the ELTE375 scientific celebration activities.





**Editorial Address**
*H-6701 Szeged, Hungary*
*P.O. Box 651*
*E-mail: asviroda@geo.u-szeged.hu*

The Acta Mineralogica-Petrographica is published by the Department of Mineralogy, Geochemistry and Petrology, University of Szeged, Szeged, Hungary





ISBN 978-963-306-039-1


---

*On the cover: Scheelite, Příbram (Czech Republic), width of the picture 23 mm. Photo and courtesy of Jiří Sejkora.*

Acta Mineralogica-Petrographica, Field Guide Series, Vol. 7, pp. 1–23.

ACTA Mineralogica Petrographica

# Příbram and Kutná Hora mining districts – from historical mining to recent environmental impact

Vojtěch Ettler[1a*], Jiří Sejkora[2b], Petr Drahota[1c,3], Jiří Litochleb[2d], Petr Pauliš[4e], Josef Zeman[5f], Milan Novák[5g] and Jan Pašava[6h]

[1] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43, Praha 2, Czech Republic; [a]ettler@natur.cuni.cz, [*]communicating author; [c]drahota@natur.cuni.cz

[2] Department of Mineralogy and Petrology, National Museum, Václavské nám. 68, 115 79 Praha 1, Czech Republic; [b]jiri_sejkora@nm.cz; [d]jiri.litochleb@nm.cz

[3] Institute of Geology, Academy of Science of the Czech Republic, Rozvojová 269, 165 00 Praha 6, Czech Republic

[4] Smíškova 564/7, 284 01, Kutná Hora, Czech Republic; [e]petr.paulis@post.cz

[5] Department for Geology, Masaryk University, Kotlářská 2, 611 27, Brno, Czech Republic; [d]jzeman@sci.muni.cz; [g]mnovak@sci.muni.cz

[6] SGA – Society of Geology applied to Mineral Deposits and Czech Geological Survey, Klárov 3, 118 21 Praha 1, Czech Republic; [h]jan.pasava@geology.cz

## Table of contents

## Introduction

The CZ3 field trip is devoted to two known polymetallic mining district, Kutná Hora and Příbram, mined since the Middle Ages, with emphasis on the long-term environmental consequences. The location of both sites in the Czech Republic and a schematic geological map of the Bohemian Massif are shown in Fig. 1

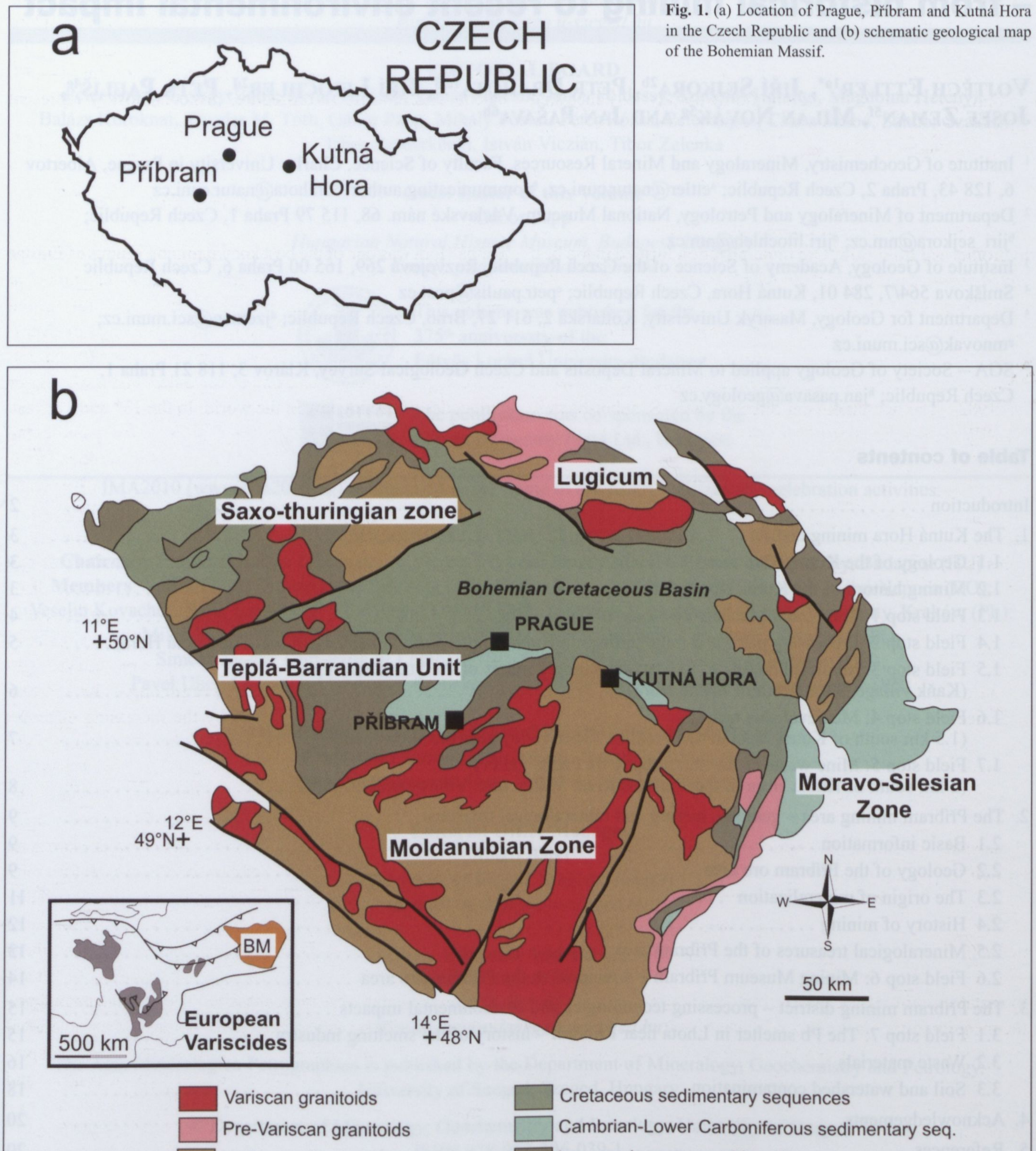



**Fig. 1.** (a) Location of Prague, Příbram and Kutná Hora in the Czech Republic and (b) schematic geological map of the Bohemian Massif.

# 1. The Kutná Hora mining district

## 1.1 Geology of the Kutná Hora area

Ore deposits in the Kutná Hora area are related to the post-magmatic mineralization of the middle Variscan granite plutonism (Figs. 1–2, Lower Permian; Bernard, 1967). During the final phase of the intrusion of the Moldanubian Pluton (Fig. 1), its axial part was uplifted and a system of fissures was formed in the area of the Kutná Hora ore district (Holub *et al.,* 1982). Lamprophyres and isolated granodiorite porphyries penetrated along the tension structures of this system. In the same field of stress, tourmaline and quartz veins and veinlets (in places with cassiterite) were formed (Losert, 1968). After release of stress in the axial part of the dome, subsidence occurred and the older system of fissures was rejuvenated and utilized again by hydrothermal fluid flow. Ore mineralization formed in the best suited segments of the system, which are represented by breccia structures near the boundaries between the gneiss and the central migmatite complex of the Malín Formation (Gföhl Unit; Fig. 3). Zones of veins were formed in shear fissures typical of the transition from anticlines to synclines (Holub *et al.,* 1982). The dominant vein direction is N–S, subordinately NE–SW with steep dips to both the E and W; structures dipping to the west host ore mineralization whereas eastward dipping structures are characterized by only hydrothermal alteration. The length of the veins equals from several hundred meters to 3 km, occasionally up to 6 km; the extent of the veins is known to a depth of 500–600 m. The thickness of the vein zones is commonly several meters and the lateral alteration zone is up to 27 m (Koutek, 1964). The hydrothermal sulphide mineralization is mostly represented by Fe-Zn-Pb-Ag type veins. Cu and Sn are also associated with these elements in the northern part of the district; in the southern part, the presence of Sb is more typical. According to Bernard, (1961), the Kutná Hora mineralization (*k-pol* association – Lower Permian sulphide polymetallic association) shows striking similarity to the Freiberg mineralization *kb+eb* ore formations (the "kies-blendige Bleierz" formation [*kb*] and the "edle Braunspat" formation [*eb*], which are rich in sphalerite, galena rich in Ag, Ag ores, quartz and carbonates and numerous additional minerals; Baumann 1958, 1965). The early stage of ore deposition was characterized by the precipitation of a major amount of arsenopyrite together with pyrite and quartz. Intense wall rock alteration with zones from inner quartz–sericite to distal chlorite also characterizes this stage. Economically the most important is the second stage of sulphide mineralization, which is characterized by the presence of dark sphalerite containing 11–15 wt% Fe, 0.46–0.66 wt% Cd and 0.11–0.14 wt% In (Hak *et al.,* 1983). Indium is a very characteristic element for the sphalerite mineralization in the northern part of the ore district. Sphalerite was the most important mineral from the economic point of view in the 20$^{th}$ century. In addition to sphalerite, pyrrhotite and subordinate galena, stannite and chalcopyrite are the most typical minerals of the second ore stage. Minerals of the first two stages of ore deposition are typical for the vein infillings in the northern part of the district (ore zones in Kaňk). Minerals of the younger mineralization stages such as Pb-Sb sulphosalts (jamesonite, boulangerite), Ag-Sb sulphosalts (pyrargyrite, miargyrite), bournonite, tetrahedrite–freibergite, berthierite, stibnite and carbonates (ankerite, kutnohorite, dolomite) are less abundant in the Kutná Hora ore zones, but they are more common in the southern part of the district. Local occurrences of fuchsite (Cr-rich muscovite), calcite and chlorite (cronstedtite, orthochamosite) represent the non-ore minerals.

## 1.2 Mining history of the Kutná Hora area

Kutná Hora was one of the best known mining centres of Europe in the Middle Ages. Consequently, the silver-rich mines at Kutná Hora were the most important economic units in the Kingdom of Bohemia. The mining boom generated the introduction of a new currency system in 1300 AD and the edition of *Ius regale montanorum*, one of the oldest and most important codes of mining law in the world. In the 13$^{th}$ and 14$^{th}$ centuries, Kutná Hora (called Mons or Chuttis) was apparently the most significant centre of silver mining in the European civilization with advanced organization and technology. By means of the so-called fire-setting technique, a depth of 500 m below the surface was reached by the exploitation of ore as early as the end of 14$^{th}$ century. Annual production of silver at that time was about 6–7 tons; about 90% of the Bohemian silver came from mining operations in Kutná Hora and approximately 3000 people worked in the local mines. The Royal Mint of Kutná Hora produced the Prague groschen, a coin used throughout central Europe. After stagnation of mining in the 15$^{th}$ century, which was probably caused by the increasing expenses related to mining at greater depths and also by devastation and inundation of mines during the Hussites wars (1419–1436), a "new boom" started before the end of the 15$^{th}$ century. The mines in the centre of the town were not reopened and mining activity moved to the southern part of the Oselské ore zone (southern part of Kutná Hora) and to the Staročeské zone with silver-bearing sulphide ores (Kaňk, north of Kutná Hora) (Fig. 3). The second half of the 16$^{th}$ century witnessed the second flourishing period of silver production. Ores of the northern ore zones (*e.g.* Staročeské lode) were poorer (200–300 g/t silver) but the veins were more massive. The average annual production of silver ranged from 2 to 4 tons. Many medieval monuments preserved in the town bear witness to the prosperity at that time. Continually increasing operating costs and cheaper silver from American and German deposits led to a decline in mining in Kutná Hora at the turn of the 16$^{th}$ and 17$^{th}$ centuries. In 1722, the Royal Mint was closed and Kutná Hora became a provincial town. From 1290 until 1800, the Kutná

Hora mining district yielded approximately 2500 tons of silver; for comparison, the Freiberg mining area (Germany) produced 5290 tons and the Havlíčkův Brod mining area (located at the border between Bohemia and Moravia) produced 180 tons of silver in the same period of time.

The last development of exploitation in the district started in 1939. The building of a flotation dressing plant at the Kaňk veins was followed by the extended mining of polymetallic ores, especially Zn and Pb ores, in the Rejské and Turkaňkské lodes (Fig. 3). The northern zones of the district were exhausted in the last quarter of the 20[th] century and the last mines were closed in 1992.

## 1.3 Field stop 1: The Czech Museum of Silver at Kutná Hora

The town began in 1142 with the settlement of the first Cistercian Monastery in Bohemia, Kloster Sedlitz, brought from the *reichsunmittelbar*[1] Cistercian Waldsassen Abbey. The history of Kutná Hora is inseparably connected with the mining of silver ores. By 1260 German miners began to mine for silver in the mountain region, which they named Kuttenberg, and which was part of the monastery property. At the end of the 13[th] century, the mine at Kutná Hora was already providing about one third of European silver production. The city became the centre of coining of the "Prague groschen", which was one of the most stable currencies in medieval Europe. The wealth of the local mines, forming the basis for the power of the Bohemian kings, led to the building of a number of historical monuments in the Gothic style (*e.g.* St. Barbara Cathedral, Stone Fountain, Stone Building, Archdeacon's Church of St. Jacob, All Saints Cemetery Church-Ossuary) and less in the Baroque era

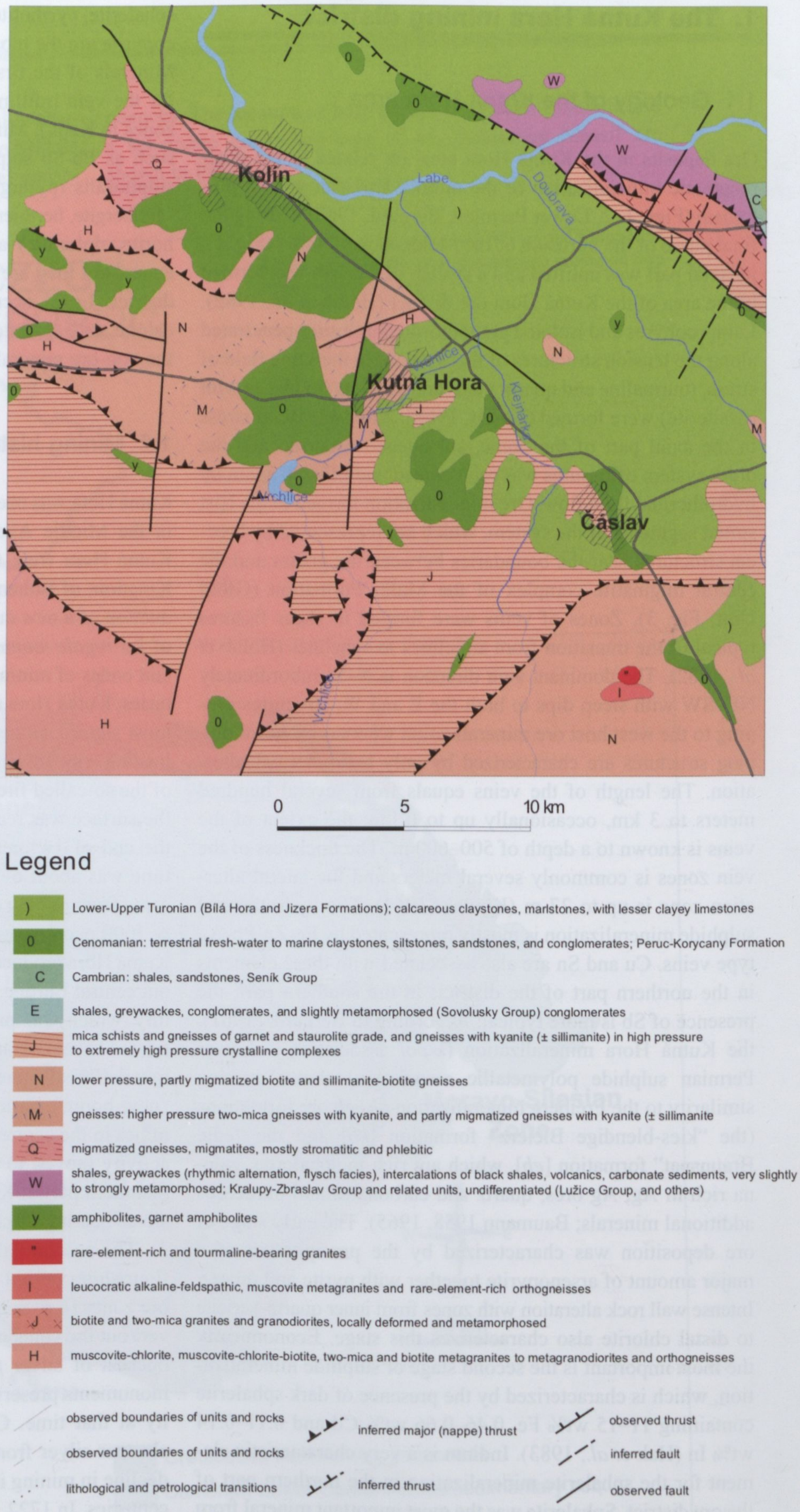


**Fig. 2.** Geological map of the Kutná Hora area.

[1] Granted with "Imperial immediacy", i.e. the abbey was under the direct authority of the Holy Roman Emperor and the Imperial Diet, without any intermediary liege lord(s).

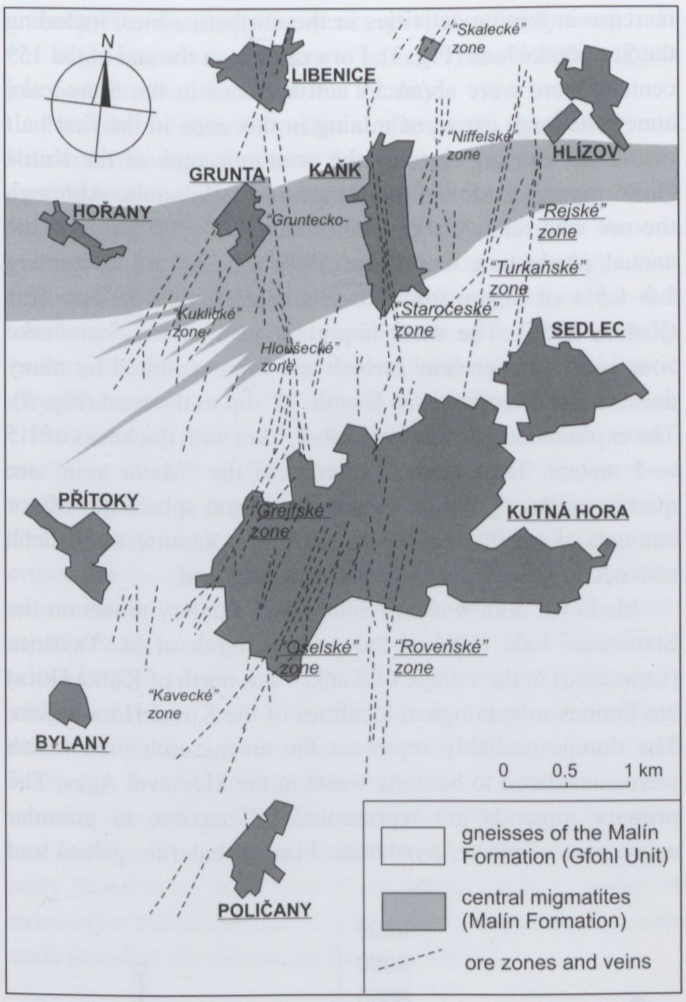



**Fig. 3.** Schematic map of the ore zones in the Kutná Hora ore district. The most important ore zones (production >100 t of silver, Kořan, 1950) are underlined.

(*e.g.* Church of St. John of Nepomuk, Convent of the St. Ursula Order, Jesuit College) leading to inclusion of the city in the UNESCO World Cultural Heritage List.

St. Barbara Cathedral in Kutná Hora is one of the most famous Gothic churches in central Europe. Construction began in 1388, but because work on the church was interrupted several times, it was not completed until 1905. The first architect was probably Johann Parler, son of Peter Parler, master builder of the St. Vitus cathedral in Prague, the capital of the Czech Republic. The outside appearance is fascinating. Originally there were eight radial chapels with trapezoidal interiors. Later on, the choir was constructed, supported by double-arched flying buttresses.

The "Hrádek" Czech Museum of Silver was originally a separate fortified guard building above the old pathway leading along the Vrchlice stream. The oldest record of this building comes from 1312, when it was reconstructed as an aristocratic residence used by the royal office. In 1490, Hrádek was purchased by the mining entrepreneur and royal official, Jan Smíšek from Vrchoviště, and the originally closed castle was changed into an ostentatious patrician residence with all the decorative features employed in the construction of this time. Several painted Renaissance ceilings as well as Gothic ribbed vaulting and wall paintings are preserved to the present day.

At the present time, the Czech Museum of Silver is located here, with an exhibition devoted to the city and to the mining and processing of silver, and also to the life style of the entrepreneurial ore-mining aristocracy. The museum is also responsible for a medieval mine discovered during the hydrogeological investigation in 1967. A 250-m long part of the medieval gallery (dated between 13th to 16th centuries) is accessible to visitors, who are equipped with a lamp, helmet and mining kirtle with a hood.

## 1.4 Field stop 2: Processing plant and mine tailings (Kaňk village, 3 km north of Kutná Hora)

In 1991, the Turkaňk mine was closed and mining operations were terminated in the district. Mine water in the adits of the Turkaňské zone was kept at a low level for 3 years. Beginning in 1994, controlled flooding of underground works in Turkaňk continued until November 2001, when the mine waters reached the dewatering adit. Until 1994, the concentrations of arsenic, iron, manganese, zinc and sulphate ions were usually relatively low. During the flooding period, the concentrations increased (1994–1996) and then decreased (1997–2001). When the mine water reached the dewatering adit in 2001, the concentrations of all the elements suddenly increased to very high levels, *i.e.* As (~80 mg/L), Fe (~6000 mg/L), Mn (~200 mg/L), and Zn (~1400 mg/L) (Fig. 4). Long-term monitoring of the physicochemical parameters of mine water from the Turkaňk shaft revealed that variations in the contaminant concentrations are related to the changes in the underground mine water regime (Kopřiva *et al.* 2005). The last period (2002–2009) is characterized by a continuous decrease in the concentrations of most of the elements except arsenic. Based on trends in the mine water geochemistry, the following conceptual model of evolution of the mine water chemistry was proposed:

a) Oxidizing conditions prevailed during mining activities and drainage of mines. Arsenopyrite was oxidized and, under oxidizing conditions, ferric iron precipitated in minerals such as amorphous ferric hydroxide, $Fe(OH)_3$(am). Released arsenic was adsorbed on ferric oxides and hydroxides. Part of the dissolved arsenic precipitated in the form of secondary minerals such as scorodite, bukovskýite, and kaňkite.

b) After closure, the mine is flooded and conditions at the bottom of the mining shaft become increasingly reducing. Arsenic is released and/or desorbed from dissolving secondary minerals and the concentrations of both arsenic and iron increase. Water chemistry stratification in the mine shaft develops in this period.

c) When the water level in the shaft reaches the de-watering drift, the layer of mine water with lower concentrations of dissolved species is discharged and therefore there is no apparent change in the water geochemistry.

d) When the interface between relatively fresh water and highly mineralized water reaches the outflow drift, there is almost a sudden change in water quality. This results in the flow of highly mineralized water with extremely high concentrations of iron and arsenic from the deeper zone to the de-watering drift (Kopřiva *et al.*, 2005; Zeman, 2008).

## 1.5 Field stop 3: Medieval dumps of Šafary and Kuntery mines of the Staročeské lode (Kaňk village, 3 km north of Kutná Hora)

The exploitation in the Staročeské zone (Fig. 3) began in the end of the 14th century, later than in the other zones of the district. The Staročeské lode contained sulphide ores with lower silver content than veins in the southern ore zones; this led to slower expansion of mining in the northern ore fields. However, the improvement of silver smelting processes in the 15th century, which required addition of base-metal sulphides, and exhaustion of the silver-rich southern zones led to a rapid increase in mining activities in the northern zones, including the Staročeské lode (Fig. 3). For example, at the end of the 15th century there were about 15 active mines in the Staročeské zone. The large extent of mining in this zone in the first half of the 16th century restored the economic rank of the Kutná Hora mining district in the Kingdom of Bohemia. Although the ore was relatively poor in silver (200–300 g/t Ag), the annual production was about 5000 tons of ore containing 1.0–1.5 t of silver from the Staročeské lode at that time (Kořan, 1950). The most important vein of the Staročeské zone is the "Major vein", which had been exploited for many decades. Its direction is N–S with 75° dip to the west (Fig. 3). The exploited length attained 1.4–1.7 km with thickness of 1.5 to 5 meters. The primary minerals of the "Major vein" are quartz, pyrite, pyrrhotite, arsenopyrite and sphalerite. Minor amounts of calcite, chalcopyrite, siderite, stannite, and galena also occur. Cassiterite is an accessory mineral.

Medieval dumps of the Šafary and Kuntery mines on the Staročeské lode (NW of the gothic church of St. Vavřinec (Lawrence) in the village of Kaňk, 3 km north of Kutná Hora) are famous mineralogical localities of the Kutná Hora region. The dumps probably represent the arsenic-rich ores which were considered to be mine waste in the Medieval Ages. The primary minerals are represented by massive to granular aggregates of pyrite, pyrrhotite, black sphalerite, galena and

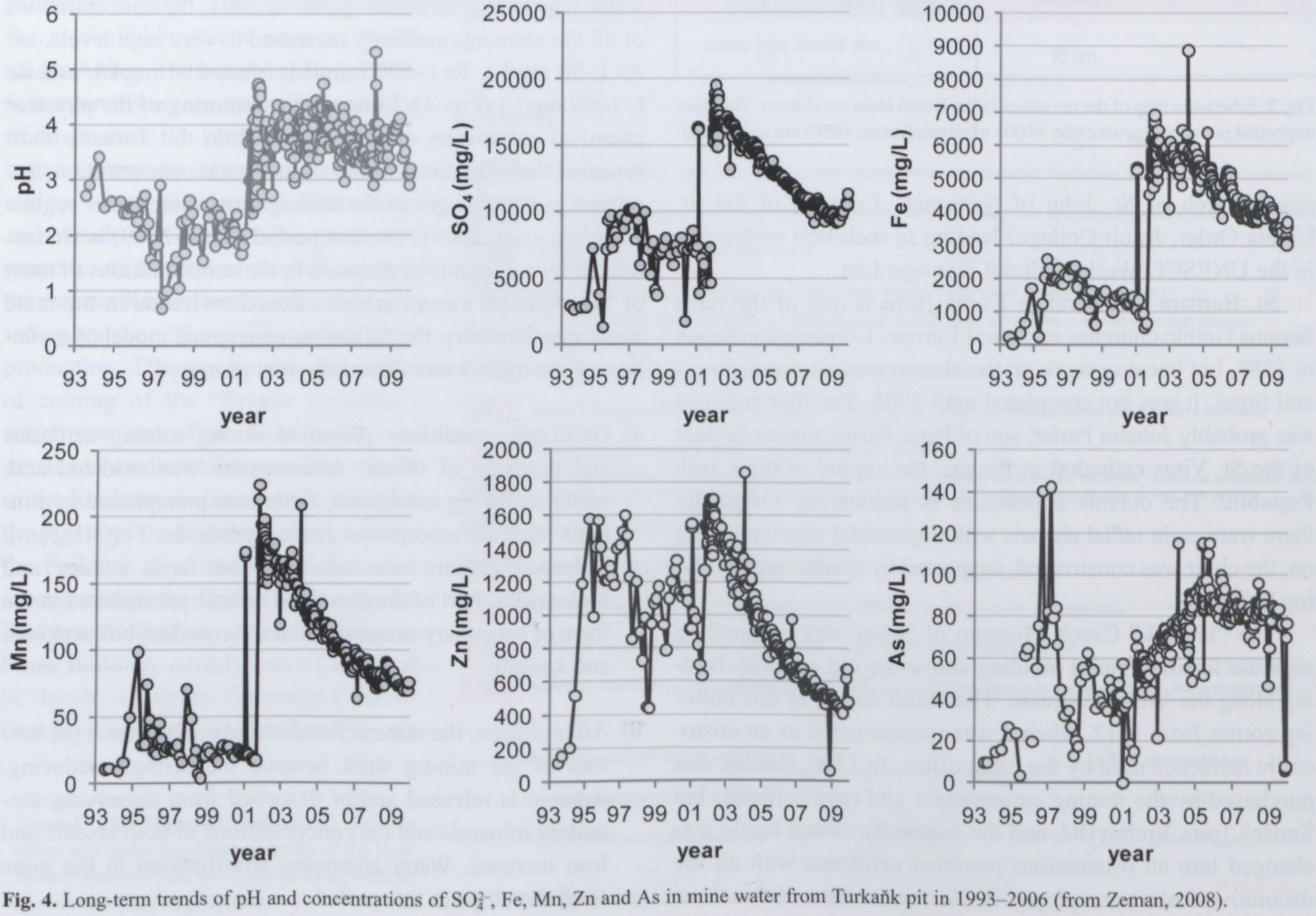



**Fig. 4.** Long-term trends of pH and concentrations of $SO_4^{2-}$, Fe, Mn, Zn and As in mine water from Turkaňk pit in 1993–2006 (from Zeman, 2008).

arsenopyrite. Arsenopyrite occurs quite abundantly as up to 1-cm large crystals in the quartz gangue. Macroscopic aggregates of stannite are rare at this locality.

Heavily weathered medieval dumps of the Šafary and Kuntery mines also represent the classic locality for secondary ferric arsenates and sulphoarsenates (Drahota & Filippi, 2009). Bukovskýite [$Fe_2(AsO_4)(SO_4)(OH)\cdot 7H_2O$], the most famous secondary mineral for the locality forms up to 1-m large cauliflower-like bulbs of yellow-green to grey-green colour that are composed of columnar microcrystals up to 0.01 mm long. In the past, this mineral was known as the Kutná Hora toxic clay (Bukovský, 1915). The mineral was studied by Novák *et al.* (1967), who classified it as a new mineral in the strunzite–beraunite group. Nearly ten years later, Čech *et al.* (1976) described a second new arsenate mineral, kaňkite [$Fe(AsO_4)\cdot 3.5H_2O$]. The mineral forms yellowish-green botryoidal coatings and crusts with thickness of several tenths of a mm to 7 mm. Another new mineral, zýkaite [$Fe_4(AsO_4)_3(SO_4)(OH)\cdot 15H_2O$], is a relatively rare secondary arsenate in the dumps and is associated with kaňkite, scorodite, pitticite, gypsum and ferric oxyhydroxides (Čech *et al.,* 1976). The mineral occurs as greyish-white nodules with up to 3 cm diameter or as infillings in cavities formed by leaching of sulphides. The last new mineral, parascorodite [$Fe(AsO_4)\cdot 2H_2O$], is one of the rarest secondary mineral found on these dumps (Ondruš *et al.,* 1999). It was originally found as an admixture in the massive pale scorodite in association with bukovskýite. The primary and secondary minerals found in the dumps are listed in Table 1.

## 1.6 Field stop 4: Medieval slag heap (1.5 km south of Kutná Hora in the Vrchlice River valley near the Vrbový mill)

The most important records of historical metallurgy in Kutná Hora are a number of slag heaps located all around the city. Slag was piled up in the proximity of the smelters, which were located in the valleys of local rivers and streams, such as the Vrchlice River and the Bylanka stream. Energy generated by water was used to operate ore stamps and bellows supplying air to the furnaces. Slag heaps in the Vrchlice River valley date back to the 15$^{th}$ to 18$^{th}$ century. The largest slag heap is situated near the Vrbový mill which was rebuilt from the Upper Royal Smelter in the middle of 18$^{th}$ century. The slag heap is about 8–10 meters high and extends for approximately 100 meters. It consists of dark-grey tapped slags with evident flow textures on their surfaces. The heap was partially re-worked, but a total volume of about 400,000 t of slag material is still present. Slag occurs in fragments from several centimetres to 30–40 centimetres in size. Remains of the furnace are present throughout the heap and consist of thermally weathered bricks, glassy surfaces and tuyeres. The chemical composition of the slag corresponds to a ferro-silicate mass (in wt%): 35.7–39.4% $SiO_2$, 33.3–44.1% FeO, 0.3–0.4% MnO, 0.6–0.9% $Al_2O_3$, 7.2–18.2% CaO, 3.9–4.9% MgO, 0.9–1.2% $K_2O$, 3.0–5.0% S, 1.71–3.27% Zn, 0.20–0.24% Cu (Manasse & Mellini, 2002). The majority of the metals are bond to silicates or oxides. Minor amounts of metals in the slag are in native forms (copper, lead) and alloys or are bonded in the residual sulphides (*e.g.* sphalerite). Based on the bulk composition of slag and on existing calibrations, Manasse & Mellini (2002) estimated temperatures of 1150–1300 °C for the slag melt in the Kutná Hora furnaces. The relatively low viscosity index of the slag (as low as 1.09–1.35) corresponds to high viscosities, which suggest less effective gravity separation of the metal from the silicate; thus metal extraction was probably incomplete at that time.

The main mineralogical component of the slag is represented by a silicate glass-like matrix, skeletal hematite and recrystallized quartz. During metallurgical processes, olivine-group (fayalite) and melilite-group (gehlenite, åkermanite, hardystonite) phases crystallized in the matrix. Minor abundances of willemite, troilite, wurtzite, magnetite, spinel minerals, wüstite and relicts of sphalerite and pyrrhotite were also detected in the slags, with higher contents of copper. Trdlička (1964) also described occurrences of rare native copper, cuprite, and tenorite in the slag material.

Weathering of the slag led to the formation of secondary phases containing Cu, Zn, Ca, etc. The most common secondary mineral is blue-green chrysocolla and small crystals of gypsum. Azurite, green malachite, grey-white smithsonite and hemimorphite are less common secondary minerals (Trdlička, 1963). Pauliš *et al.* (1998) found dark red coatings of alacranite, up to 0.5-mm long needles of dark green brochantite and small aggregates of willemite and zincite, chalcocite, djurleite, troilite and lead. The total list of minerals detected in the slag is given in Table 2.

**Table 1.** Primary and secondary minerals from the medieval dumps of Šafary and Kuntery mines of the Staročeské vein, Kutná Hora ore district (Pauliš, 1998; Sejkora *et al.,* 2002a). The mineral names in bold represent new minerals described from the Kutná Horá ore district.

| | | | | |
|---|---|---|---|---|
| alacranite | calcite | gypsum | pitticite | siderite |
| allargentum | cassiterite | jarosite | pyrrhotite | sphalerite |
| aluminite | chalcanthite | **kaňkite (1976)** | pyrite | stannite |
| alunogen | chalcopyrite | marcasite | quartz | **zýkaite (1978)** |
| arsenopyrite | Fe oxyhydroxide | melanterite | rozenite | |
| **bukovskýite (1967)** | galena | **parascorodite (1999)** | scorodite | |

**Table 2.** Primary and secondary minerals from the slag dump in the Vrchlice river valley, Kutná Hora ore district (Pauliš, 1998).

| | | | | |
|---|---|---|---|---|
| ackermanite | cuprite | hematite | pitticite | spinel |
| alacranite | djurleite | hemimorfite | plumboferrite | tenorite |
| azurite | fayalite | hydrozincite | pyrrhotite | troilite |
| brochantite | Fe oxyhydoxide | jarosite | quartz | willemite |
| chalcocite | gehlenite | lead | serpierite | wurtzite |
| chrysocolla | gypsum | magnetite | sphalerite | wüstite |
| copper | hardystonite | malachite | smithsonite | zincite |

## 1.7 Field stop 5: Mine waste at the St. Anthony de Padua gallery (2 km south of Kutná Hora in the Vrchlice River Valley near Vrbový mill)

There are several exploration and mining galleries preserved in the Vrchlice River valley, south of Kutná Hora. For example, the oldest mine map known from the Kutná Hora ore district is the map of the Poličany gallery (2.5 km south of Kutná Hora) (Fig. 5). It is the second oldest mining map known in Central Europe from 1534; the oldest mine map (from 1529) originates from the Freiberg ore district (Malec, 1997). The largest mining work in the Vrchlice River valley is the gallery of St. Anthony de Padua. It was named after the homonymic company of miners that started exploiting the gallery in 1752. The first ore yields were very promising, because the gallery followed an up to 0.7 m thick vein rich in Ag and Sb (the grade of Ag was estimated at 4100 g/t, Kořan, 1950). However, mining operations were terminated 3 years later, because the vein split downward into several branches. The second short mining episode occurred in 1769–1770 and the last in 1943–1945. During the latter period of mining, operations were promising at the beginning because a vein crossing with silver-bearing sulphoantimonates in the gallery length of 60 m was exploited. The quartz vein pinched out after 65 m and then the gallery continued in the N–S direction along the 5-cm thick mylonite structure with dispersed Sb mineralization (stibnite, berthierite; Koutek & Kutina, 1949). The total length of the gallery is 326 m.

Some primary ore minerals of the mine can still be found in the gallery and in the mine dump close to the gallery. These minerals are represented by gangue minerals, such as massive quartz and Ca-Mn carbonates. The composition of carbonate mostly corresponds to kutnohorite [$Ca(Mn,Mg,Fe)(CO_3)_2$]. The major ore mineral is dark steel-grey berthierite, forming granular, fibrous and acicular aggregates in the quartz gangue. Small aggregates and crystals of sulphides (pyrite, arsenopyrite, galena, sphalerite, etc.) are abundant in quartz as well as in the carbonate gangue. Silver-bearing minerals are quite rare. The most common Ag-bearing mineral is miargyrite [$AgSbS_2$], forming aggregates up to 10 mm in size or short columnar crystals. The rarer Ag-bearing minerals are steely-

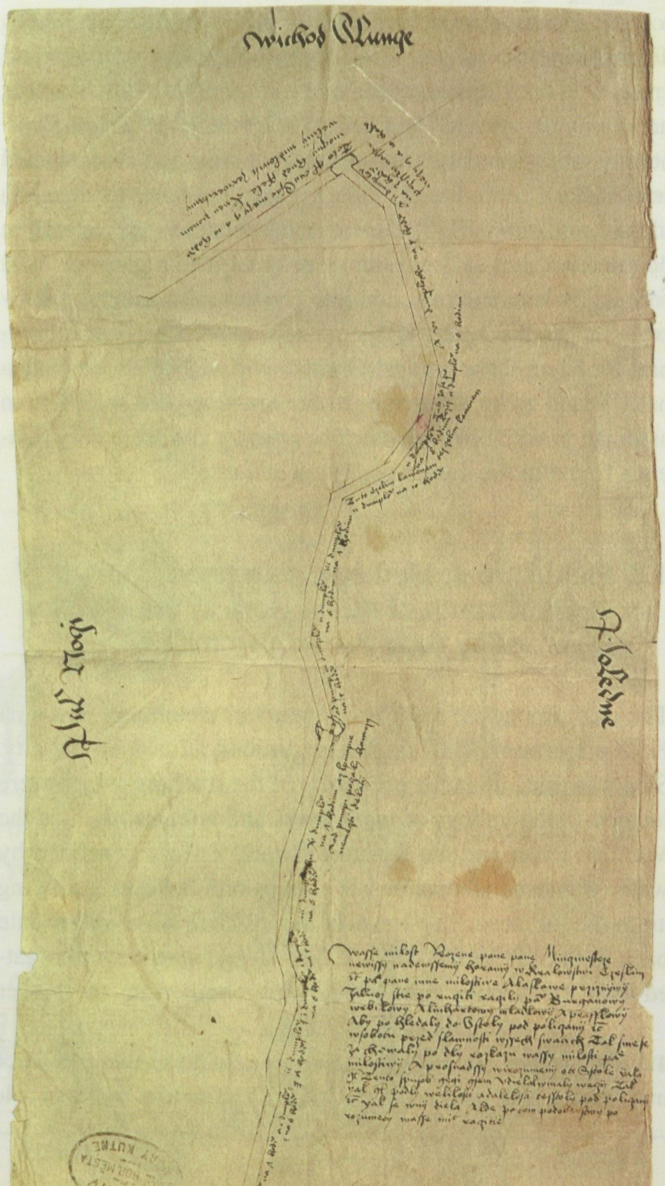


**Fig. 5.** The oldest mine map of Kutná Hora: the Poličany gallery in 1534 (Zikmund Prášek).

**Table 3.** Minerals from the gallery of St. Anthony de Padua, Kutná Hora ore district (Pauliš 1998; Sejkora *et al.*, 2002b). Kutnohorite as a new mineral was described from the dumps of the nearby Bylanka River Valley close to this locality.

| | | | | |
|---|---|---|---|---|
| acanthite | calcite | galena | pyrargyrite | sphalerite |
| almandine | cervantite | gypsum | pyrrhotite | stephanite |
| anatase | chalcopyrite | jamesonite | pyrite | stibnite |
| andorite | diaphorite | **kutnohorite (1901)** | pyrostilpnite | tintinaite |
| argentite | dolomite | marcasite | quartz | valentinite |
| arsenopyrite | electrum | miargyrite | senarmontite | |
| berthierite | freibergite | muscovite (Cr-rich) | siderite | |
| boulangerite | freieslebenite | proustite | silver | |

grey diaphorite [$Pb_2Ag_3Sb_3S_8$] forming up to 3-mm long grooved crystals in cavities of quartz, lead-grey freieslebenite [$AgPbSbS_3$] (short columnar crystals up to 2 mm in size), and red-orange pyrostilpnite [$Ag_3SbS_3$] (up to 4 mm in size, shiny tabular crystals). The list of minerals known from this locality is given in Table 3. In addition to primary and secondary ore minerals, the surrounding rock contains the minerals of the alpine paragenesis (dipyramides of anatase, tabular crystals of brookite) that can also be found in the rocks in the gallery and mine dump.

## 2. The Příbram mining area – geology, mining and mineralogical treasures

### 2.1 Basic information

The Příbram ore area is one of the most important regions of hydrothermal ore mineralization of the Czech Republic. Total production of metals from this area was 3800 t Ag, 518,000 t Pb, 70,000 t Sb (Příbram base-metal ore district) and 48,400 t U (Příbram uranium ore district). In 1875, the Vojtěch mine was the first mine of the world to reach a vertical depth of 1000 m; the more than 1800 m depths of mining in the uranium ore district are among the greatest in Europe. The ore deposits of the Příbram ore area had a long history of mining of silver and base-metal ores: the beginning of mining dates back to the Middle Ages. The objective of this field stop is to visit this site known for occurrences of numerous mineral species and to discuss the long-term environmental impact of anthropogenic activities related to mining.

### 2.2 Geology of the Příbram ore area

The region of Central Bohemia (Czech Republic) belongs to the classic areas of economically significant hydrothermal mineralizations (Příbram – base metals and uranium, Jílové – gold and Kutná Hora – silver and base-metal mineralization; Velfl *et al.*, 2007). The ore deposits of the Příbram ore area are located near the boundary of the Teplá–Barrandian Unit (Upper Proterozoic, Cambrian) and the Central Bohemian Pluton (Figs. 1, 6–7). In this area, two main ore districts are distinguished on the basis of their geological positions and characteristics of hydrothermal mineralization: a silver-bearing base-metal ore district and a complex uranium-bearing ore district (Litochleb *et al.*, 2003; Fig. 6).

The Příbram base-metal ore district is represented by the main deposits of Březové Hory and Bohutín, accompanied by further smaller deposits and occurrences. The hydrothermal ore veins of these deposits penetrate the Upper Proterozoic slate and Cambrian sandstone and greywacke, especially along the NE–SW oriented “Clay Fault”. These veins are mostly oriented in the N–S direction; shorter NW–SE striking veins also occur in the shallow zones (Bernard, 1991). The ore veins at the Březové Hory deposit follow the course of basalt dykes of Early Paleozoic age (Fig. 8). They have been mined within an area of about 10 km$^2$. 43 veins are known in the shallow zones, whereas there are 5-6 main veins at depth. The most significant

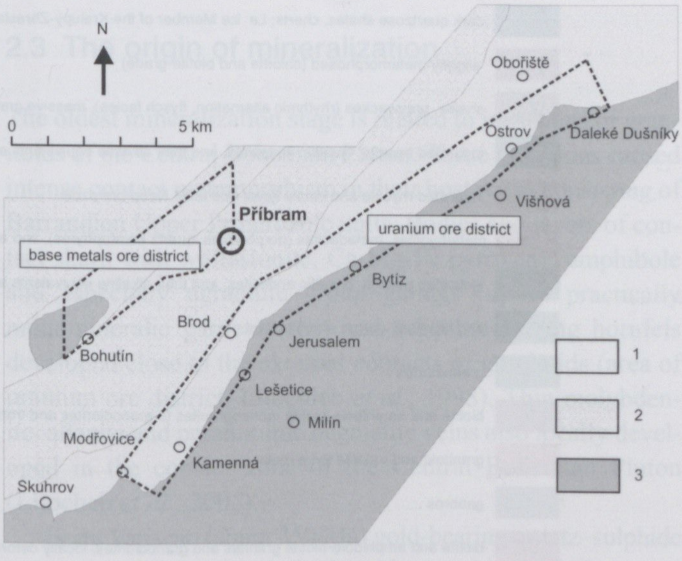
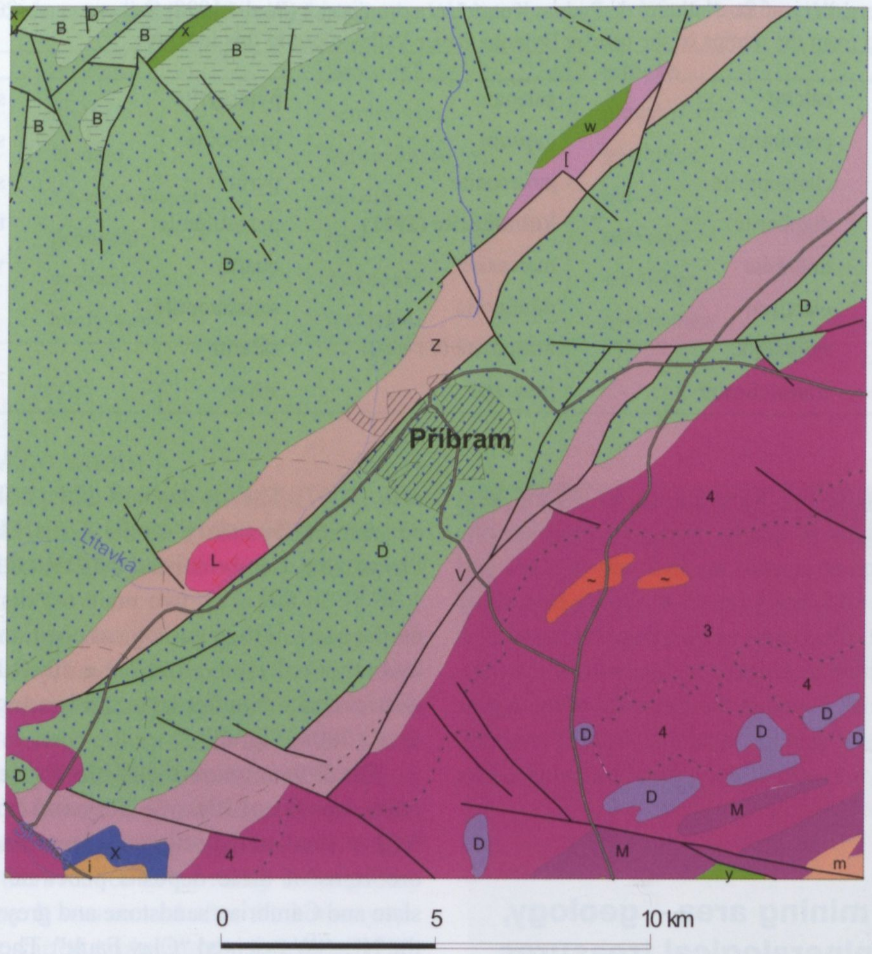



**Fig. 6.** The Příbram ore area, central Bohemia, Czech Republic.
*1 – Upper Proterozoic; 2 – Cambrium; 3 – granitoids of the Central Bohemian Pluton.*

**Fig. 7.** Geological map of the Příbram area.



is the Main Vojtěch vein, which is about 1 to 2 m thick; however, it is exceptionally 6 m thick or even thicker. It has a length of 3.5 km and was followed to depth to 1580 m below the surface (41 levels) by the Vojtěch and Prokop shafts (Fig. 8). At middle depths, the monomineralic parts of this vein with Ag-bearing galena were as much as 70 cm thick. The average grade was 450 g/t of Ag, and the specific grade was 0.6 kg of silver per m² in the plane of the vein. In the deeper part of the deposit, the ore mineral infillings of veins contain abundant "hard ore", which consists of fine-grained quartz with disseminated pyrite, galena, sphalerite, boulangerite and Ag minerals.

The ore veins at the Bohutín deposit transect the Bohutín amphibole-biotite quartz diorite, the oldest component of the early Variscan magmatism of the Central Bohemian Pluton. Klementská vein, the most important vein of the Bohutín deposit was mined to a depth of 1350 m along a 2-km long section. The characteristic "hard ore" known from the Březové Hory deposit was not developed here, but younger antimony mineralization (stibnite, berthierite) mineralization was mined out at this deposit. The youngest uraninite–carbonate stage (uraninite, Ni-Co-Fe arsenides) and also sphalerite and silver ores are characterized by irregularly mineralized veins of the smallest deposit (Černojamské) in this ore district.

More than 160 mineral species are known from the Příbram base-metal ore district. Many minerals occurred here in very well-developed forms displaying extraordinary variability of crystal shapes, types of twinning and colours (Ag minerals, calcite, barite etc.).

In spite of the relative abundance of silver minerals (22 species, especially native silver, argentite, pyrargyrite, stephanite and freibergite), the most important source of this metal was the Ag-rich galena; however, other sulphide minerals like sphalerite, bournonite and boulangerite also contained high amounts of silver due to their microscopic intergrowths with Ag minerals.

The complex uranium-(base-metal) ore district at Příbram represents the largest accumulation of vein-type hydrothermal uranium ores in the Czech Republic and is comparable to world-class deposits of this type. Uranium mineralization is bound to a 1–2 km wide and almost 25-km long zone formed by a strongly tectonized zone of Upper Proterozoic rocks along the contact with granitoids of the Central Bohemian Pluton (Figs. 6–7). The central part of this district, between the Lešetice and the Bytíz deposit, concentrated more than 98% of the total uranium production; 52% of the uranium ore was extracted from the richest Bytíz deposit that comprised 584 mineralized veins. The main vein structures were traced for 2.4–2.7 km along their extension and to a depth of 1.1–1.4 km under present surface. More than 210 mineral species were found there. The main economic ore consisted of uraninite together with some coffinite and U-bearing antraxolite (a bituminous substance). The lens-shaped ore bodies reached up to 0.3 m in width and were almost 20 m² in size. Parts of the legendary Bt4 vein in the Bytíz deposit exhibited a specific grade of 60–100 kg of uranium per m² in the vein plane.

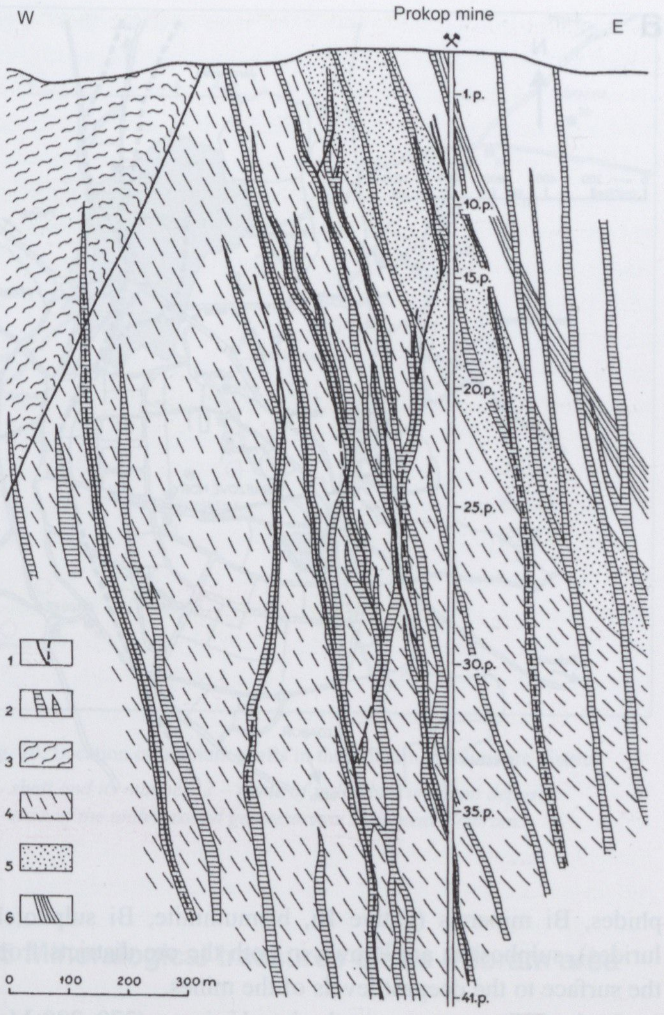


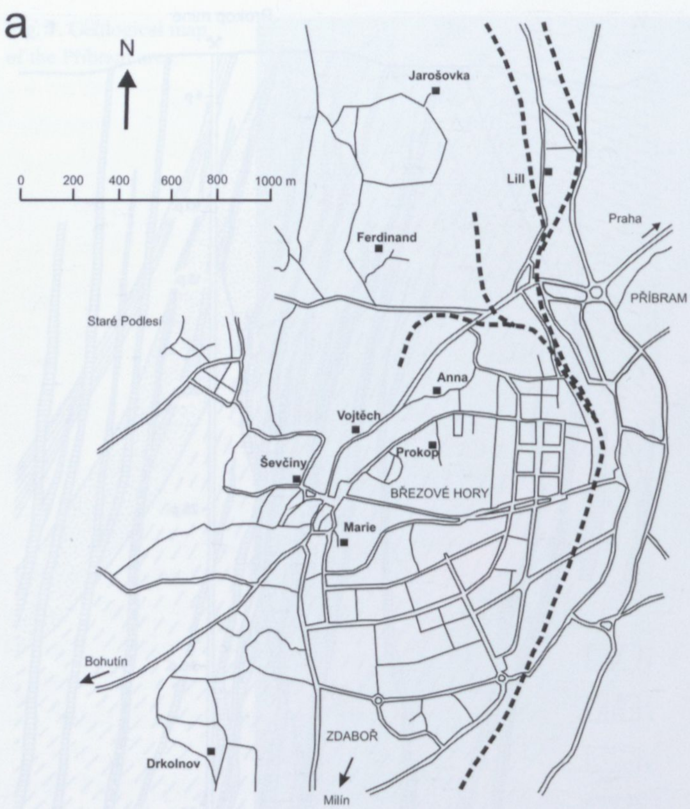

**Fig. 8.** Geological cross-section of the Březové Hory deposit, Příbram (according to Bernard, 2000).

*1 – ore veins; 2 – Early Paleozoic basalt dykes; 3 – Upper Proterozoic; 4 – Cambrian sandstones; 5 – Cambrian greywackes; 6 – Cambrian shales.*

## 2.3 The origin of mineralization

The oldest mineralization stage is related to intrusions of granitoids of the Central Bohemian Pluton. These intrusions caused intense contact metamorphism in their host rocks consisting of Barrandian Upper Proterozoic units. Bodies and layers of contact skarn with wollastonite, Ca-Mg-Fe pyroxene, amphibole and especially ugrandite group garnets (up to practically monomineralic garnet rocks) and scheelite-bearing hornfels developed close to the external contacts of granitoids (area of uranium ore district, Litochleb *et al.*, 1998). Thin molybdenite–allanite and peraluminic pegmatite veins also locally developed in the contact zone of the Central Bohemian Pluton (Litocheb *et al.*, 2005).

Early Variscan (about 350 Ma) gold-bearing quartz–sulphide vein mineralization is relatively widespread in the Příbram ore area but its economic significance is minimal. The occurrences of quartz veins and veinlets with fine-grained gold, sul-



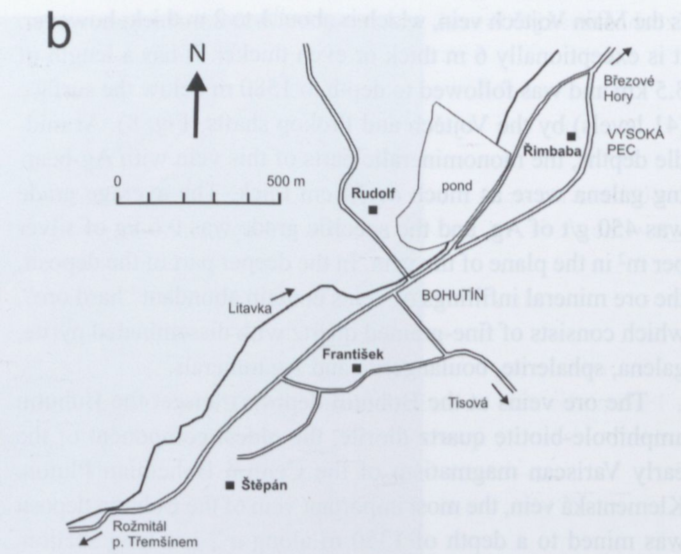




**Fig. 9.** Location of main shafts in the base metals ore deposits Březové Hory, Černojamské (a) and Bohutín (b) (according to Škácha & Plášil, 2002).

phides, Bi minerals (native Bi, bismuthinite, Bi sulphotellurides), sulphosalts are known in both the ore districts from the surface to the deepest levels of the mines.

In the Příbram ore area, the late Variscan (270–290 Ma) vein-type base-metal and uranium mineralization is the most significant. These types were developed in both ore districts distinctly and with different intensity depending on the geological and structural conditions. The hydrothermal processes of vein formation were classified into several stages in the temperature range of 300–70 °C.

In the Příbram base-metal ore district, the older base-metal stage dominates. It is represented by quartz–siderite–calcite veins with galena, sphalerite, pyrite, tetrahedrite, bournonite, boulangerite, and Ag minerals etc., with occurrences of well-formed crystals of these mineral species. A younger barite-stibnite stage developed only in the Klementská vein of the Bohutín deposit. The youngest uraninite–carbonate stage (uraninite ± coffinite, Ni-Co-Fe sulphides and arsenides) is known at the Černojamské deposit (Lill mine) and only very locally at the Březové Hory (Jánská vein) and Bohutín (Severozápadní Řimbabská vein) deposits (Litochleb *et al.*, 2000b; Škácha *et al.*, 2009) (Fig. 9).

In the Příbram uranium ore district, base-metal (siderite–quartz veins with galena and sphalerite) mineralization also occurs in the oldest siderite–sulphide stage. The predominance of calcite (with several generations) is characteristic for the superimposed stages. Abundant uraninite aggregates were formed in the calcite–uraninite stage. The origin of uranium-bearing antraxolite was connected with the youngest calcite–sulphide stage, which is also characterized by occurrences of coffinite and montroseite, sulphides, arsenides, sulphosalts, selenides, native silver and silver minerals, zeolites and whewellite (Litochleb *et al.*, 2002, 2004). This youngest stage is considered to be the result of remobilization from the earlier stages. The origin of monometallic accumulations (bonanzas) of extremely rich silver ores (*e.g.* Brod deposit, shaft No. 6 or Háje deposit, shaft No. 21) (Fig. 10) is also assumed in this youngest stage.

## 2.4 History of mining

In spite of the fact that mining in the Příbram base-metal ore district started already in the 13th century, almost 97% of all reserves has been exploited during the last 170 years, between 1810 and 1980. The main prosperous period of mining began here in the second half of the 18th century due to technical improvements introduced by *Bergmeister* (mine inspector) J.A. Alis (opening of mines by deep vertical shafts, construction of a new smelter and water reservoirs and races). In 1779, the Vojtěch mine, the first vertical shaft was opened, and four mines (Anna, Ševčiny, Marie and Prokop) followed shortly afterwards (Fig. 9a). In 1875, the Vojtěch mine was the first mine in the world to reach a depth of 1000 m. Almost 100 years later (1966), the Prokop mine reached a maximum depth of 1597.6 m as the first mine of this depth in the former

Czechoslovakia (Figs. 8 and 9a). The individual mines of the Březové Hory and Bohutín deposits were interconnected by the main 9 km long drainage gallery (completed between 1789 and 1859) and additional adits with a total length of 19 km. The Bohutín ore deposit was opened by the Rudolf, Štěpán and Řimbaba main shafts; it was mined down to a depth of 1350 m below the surface (Fig. 9b) (Bambas, 1990; Tvrdý, 2003).

First silver and later lead were the principal extracted metal components of the ores, with other by-products such as zinc and, to a lesser extent, antimony and gold improved the economy of mining. Mining of the Březové Hory deposit was finished in 1978 and of the Bohutín deposit in 1980. Almost 22 million tons of ore with 3837 tons Ag, 517,961 tons Pb and 70,300 tons Sb have been mined during the whole period of exploitation of the district. 58% of the total amounts of silver and at least 90% of the total amount lead which have been extracted in Czech territories have been mined from this district.

Exploration of uranium ores in the present Příbram uranium ore district started in 1947. Almost 60 economic occurrences were located within the 50-km$^2$ large area. The mining period started by opening the first shafts (No. 1 and 2 – Vojna) in 1948. During the first decade, the vein system was explored to a depth of 500 m from 20 new shafts. A relatively short time between the discovery of the first indicators of uranium anomalies (1947) and the beginning of extraction (1950), together with the extraordinary scale of the ore bodies, qualified the Příbram uranium ore district for competition with the most important ones in the world. Uranium mining culminated in 1975, when this ore district became the main producer of uranium ores in the former Czechoslovakia. More than 2500 carbonate veins were found and prospected within this ore district formed by a number of individual ore deposits (*e.g.* Kamenná, Lešetice, Brod, Háje, Bytíz). The uranium mineralization occurred in 1641 veins, base metals mineralization in 35 veins and finally monomineralic silver mineralization in 19 veins. In 1976, the final depth 1838.4 m was reached in shaft No. 16 (Háje). At that time, this was the deepest vertical ore mine in Europe.

The extraction of uranium ores in the ore district was terminated in the Dubenec mine in September 1991. Between 1992 and 1998, an underground gas reservoir with a capacity of more than 620,000 m$^3$ was built from the 21$^{st}$ level (about 1000 m under surface) of shaft No. 16 (Háje). This reservoir was formed by 107 interconnected storage tunnels with a total length exceeding 45 km (Litochleb *et al.*, 2000a). Now mining in the uranium ore district is can be seen from 27 large mine dumps, part of which are used as resources for production of crushed and sorted rocks.

The following numbers indicate the remarkable extent of the mine works in the uranium ore district of Příbram: 23 km of shafts, 2188 km of horizontal adits and 300 km of chutes were created in an area of 57.6 km$^2$ over 44 years (1948–1991). The total production of 48,432 t of pure U metal represented 49% of Czechoslovak production since 1945. The parallel extraction of base metals and silver from veins produced more than 6000 t Pb, 2400 t Zn and 28 t Ag (Litochleb *et al.*, 2003).

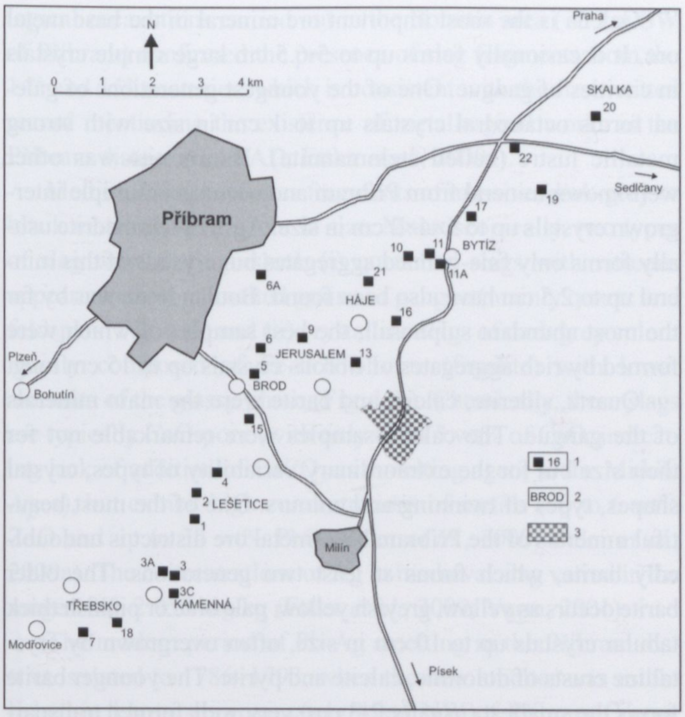



**Fig. 10.** Location of uranium shafts in the Příbram uranium ore district.
*1 – shaft and its number; 2 – name of individual uranium deposit; 3 – area of the underground gas reservoir Háje near Příbram.*

## 2.5 Mineralogical treasures of the Příbram area

In addition to the economic, historical, geological and mineralogical importance of the deposits of the Příbram ore area described above, these deposits are also world famous as sources of a large number of high-quality mineral samples, which are presented in many museums and private collections (Škácha & Plášil, 2002). The most complete collection of mineralogical samples from both ore districts is deposited in the Mining Museum of Příbram; a great many high-quality samples can also be found in the excellent mineralogical collections of the National Museum in Prague.

In the Příbram base-metal ore district, silver minerals are quite abundant (Sejkora & Litochleb, 2003a). Native silver forms rich irregular and wire-like aggregates and sheets with up to 7 cm in size, often together with aggregates, pseudomorphs and crystals of argentite up to 2 cm in size. Beautiful, dark red pyrargyrite (up to 2.5 cm), columnar stephanite (up to 4 cm) and thin tabular polybasite (up to 1 cm) crystals were also locally abundant. On the other hand, red proustite (up to 2 cm) and elongated tabular pyrostilpnite crystals were very rare. Diaphorite represented the main Ag-bearing mineral of the "hard ore" and was common as microscopic grains in galena. Its striated, up to 1 cm long columnar crystals were rare and belong among the best in the world. Similar freieslebenite crystals up to 0.5 cm in size were found in association with acicular crystals of owyheeite.

Galena is the most important ore mineral in the base metal ore. It occasionally forms up to 5-6.5 cm large simple crystals in cavities of gangue. One of the youngest generations of galena forms octahedral crystals up to 1 cm in size with strong metallic lustre (called steinmannite). Bournonite was other well-known mineral from Příbram and occurs as multiple intergrown crystals up to 5×4×2 cm in size. Ag-rich tetrahedrite usually forms only fine-grained aggregates but crystals of this mineral up to 2.5 cm have also been found. Boulangerite was by far the most abundant sulphosalt, the best samples of which were formed by rich aggregates of fibrous crystals up to 15 cm long.

Quartz, siderite, calcite and barite were the main minerals of the gangue. The calcite samples were remarkable not for their size but for the extraordinary variability of types, crystal shapes, types of twinning and colours. One of the most beautiful minerals of the Příbram base-metal ore district is undoubtedly barite, which forms at least two generations. The older barite occurs as yellow, greyish yellow, pale blue or pinkish thick tabular crystals up to 10 cm in size, often overgrown by crystalline crusts of dolomite, calcite and pyrite. The younger barite forms the smallest (usually 2-3 cm) very well-formed transparent columnar crystals with large colour variability: colourless, white, pale blue, bright yellow, pink or red. Yellow to brown lenticular siderite crystals up to 3 cm in size and a red-brown variety of goethite forming aggregates and crusts with a typical velvet surface also belong to characteristic minerals here.

Very interesting minerals are also known from the oxide zone of the deposit (Sejkora & Litochleb, 2003b). The white, yellow, grey and dark coloured crystals of cerussite with size of up to 2 cm and the whitish to yellow hexagonal crystals of mimetesite up to 1 cm in size are among the most spectacular species. The most beautiful supergene mineral is the pyromorphite, which forms elongated or thick columnar crystals, usually up to 2 cm in size. Pyromorphite crystals are frequently grown to rich druses on strongly limonitized gangue. The majority of pyromophite crystals are green to remarkably bright green in colour; bright yellow or brown crystals are rare.

A great many interesting mineral samples also characterize the Příbram uranium ore district (Růžička, 1986; Sejkora & Litochleb, 2003a). The most significant finds are the native elements. Superb samples of native silver were found at several deposits (*e.g.* Háje, Brod). The irregular, columnar or wire-like silver aggregates in the calcite gangue weighed up to tens of kg and silver wires up to 10 cm long were also occasionally found. Pseudomorphs of native silver after dyscrasite crystals up to 7 cm in length also occurred. Stibarsen and arsenic were relatively abundant in some parts of the veins (Háje, Brod, Bytíz, Třebsko deposits), where they formed stratified hemispherical aggregates up to 15–20 cm in size. A large lens with thickness to 25 cm in a 3×3 m plane of pure native antimony were found in the calcite vein of the Bytíz deposit. It yielded pure native antimony samples with weight of up to 10 kg and rarely also trigonal crystals up to 1 cm in size. Mineralogically unique accumulation of dyscrasite crystals originated from the Háje deposit (shaft No. 21). Columnar crystals of dyscrasite 1–8 cm in length or skeletal aggregates up to 3×6 cm in size were always enclosed in aggregates of native arsenic. Another type of dyscrasite is known from the Brod deposit (shaft No. 15) where it formed granular aggregates up to 10–12 cm in size in the siderite–calcite gangue (Kolesar, 1990; Knížek *et al.*, 1990).

Uraninite was the prevailing uranium mineral in the uranium ore. It forms black reniform (up to 20 cm in size) or spherical aggregates, veins and massive lens in older carbonate gangue. In the Kamenná, Brod and Bytíz deposits, the thickness of massive uraninite lenses reached up to 10–20 cm (exceptionally 50–100 cm) and their plane had an area of up to 20 m$^2$. The most abundant mineral in the veins was calcite, which occurred in six generations. Large druses of calcite crystals were abundant in open spaces of veins; the plane of these cavities had an area of 20–40 m$^2$ (exceptionally over 100 m$^2$) with a thickness of up to 0.5–1.4 m. The size of individual scalenohedral calcite crystals reached 40 cm. Interesting crystals of zeolites (analcime, harmotome, stilbite, heulandite) were also found in druses of veins, in a similar way as the very rare, well-developed whewellite crystals up to 8 cm in size (Knížek & Litochleb, 2005).

## 2.6 Field stop 6: Mining Museum Příbram – a window to the Příbram ore area

The Příbram Mining Museum is situated in the area of the historical mines of the Březové Hory deposit. It was originally founded as a country museum in 1886 and has collected historical and natural specimens in a wide spectrum of human activities since that time. Its depositories and exhibitions document especially mining and ore processing in two distinct ore districts of the Příbram ore area – the historical base metals ore district with abundant silver and lead mineralization and the more recent uranium ore district (Litochleb, 2003; Velfl, 2008).

The museum's exhibits were built in the original mine workings and administrative buildings and they show the rich mining past of the region (http://www.muzeum-pribram.cz).

The first part of the exhibits is located in the Ševčiny shaft and its surroundings. Here, the following exhibitions can be visited: "Mining and metallurgical buildings of the Příbram region in historical photographs", "History of mining in the Příbram region", "The development of vertical mining transport in the Příbram region" etc. and especially mineralogical collections, which include unique mineralogical and geological samples from both Příbram ore districts. The collection of silver minerals predominates in the exhibition. It is supplemented by samples of old miner's working tools, miner's tallow and oil safety lamps, miner's ceremonial sticks and homemade models of shafts. The visitors can also view the attractive authentic building of the Ševčiny shaft built in the style of industrial architecture of the 19$^{th}$ century with the mouth of the shaft with the cage used by miners and a unique view of the surroundings from the 37 m high Ševčiny tower gallery. An uncommon exhibition project arose on the mine dump of the Ševčiny shaft. Mining equipment, which was used in local mines in the second half of the 20th century, is installed on the mining railway track, which is more than 180 m long.

A unique technical monument, a steam winding engine from 1914, is one of the rarest exhibits of the Mining museum. It is situated in the engine room of the historical Anna shaft, which was opened in 1789. The shaft building of the Vojtěch shaft, which was built in 1870, is another technical attraction. The exhibition in this building is supplemented by a permanent exhibit dedicated to the achievement of the world primacy in reaching a vertical depth of 1000 m in the Vojtěch shaft in 1875. In the nearby engine room, there is another unique steam winding engine from 1889. From the forecourt of the Anna shaft it is possible to go underground by a little mining train to the 260-m long Prokop adit from 1832, which leads to the mouth of the Prokop shaft, which, with a depth of 1,597.6 m, is the deepest shaft of the Březové Hory deposit. Other mining underground areas opened for museum visitors are the 330-m long water course level between the Anna and Vojtěch shafts and a large water wheel (12.4 m in diameter) in the underground of the Drkolnov shaft.

## 3. The Příbram mining district – processing technologies and environmental impacts

### 3.1 Field stop 7: The Pb smelter in Lhota near Příbram – history of the smelting industry

The history of mining and smelting activities in the Příbram district extends far into the past. The mining and smelting of Ag-bearing ores was confirmed at these sites and dated between the end of the 13th and the beginning of the 16th century. Archaeological excavations carried out in the Bohutín area (~5 km SW of Příbram) confirmed the presence of slag fragments from the 14th and 15th centuries, which is consistent with the first written record mentioning the existence of metallurgical works in the Příbram district (1311 AD; Ettler *et al.*, 2009a).

Medieval slag occurs as fragments of massive, dark-grey or black material, several cm in size. Macroscopically, two types of slag were distinguished: (i) quenched slags with vitreous appearance with unmelted grains of gangue (mainly quartz and feldspars; Fig. 11a) and (ii) crystalline slags of dark grey colour mainly composed of Fe-rich olivine (fayalite) with lower amounts of the glassy phase (Fig. 11b). Chemically, these slags are typically CaO-poor (with only up to 5 wt% of CaO, indicating lack of addition of $CaCO_3$ as a melting agent in the Middle Ages), but exhibit high concentrations of metals (up to 6 wt% ZnO and up to 34 wt% PbO; Ettler *et al.*, 2000; Ettler *et al.*, 2009a). The concentrations of Ag in medieval slag varied in the range 10.5–2 950 mg/kg (Ettler *et al.*, 2009; Vurm, 2001).

The modern period of Pb-Ag smelting in the Příbram district is dated to 1786–1793, when the new smelter was established in Lhota, approximately 4 km NW of Příbram (Vurm, 2001). Until 1972, the smelter processed mainly Pb-Ag ores mined in the Příbram area. Whereas the peak of Pb mining occurred between 1880 and 1920, the Pb production in the smelter sharply increased after World War II (Fig. 12). From a technological point of view, Pb and Ag were produced by the reducing fusion process in a blast (shaft) furnace called a "water-jacket". The roasted ore, scrap-iron additive, limy additive ($CaCO_3$), silica source (gangue or recharge slag) and coal/coke were mixed and served as a charge for smelting in the blast furnace. A well-balanced mixture of these components helped to maintain the furnace temperature around a mean value of 1300 °C. The density and viscosity of the molten slag had to be kept low enough to ensure the gravity separation of metal-rich liquids (sulphide matte, quasi-pure molten metals) containing elevated amounts of the desired metals or metalloids

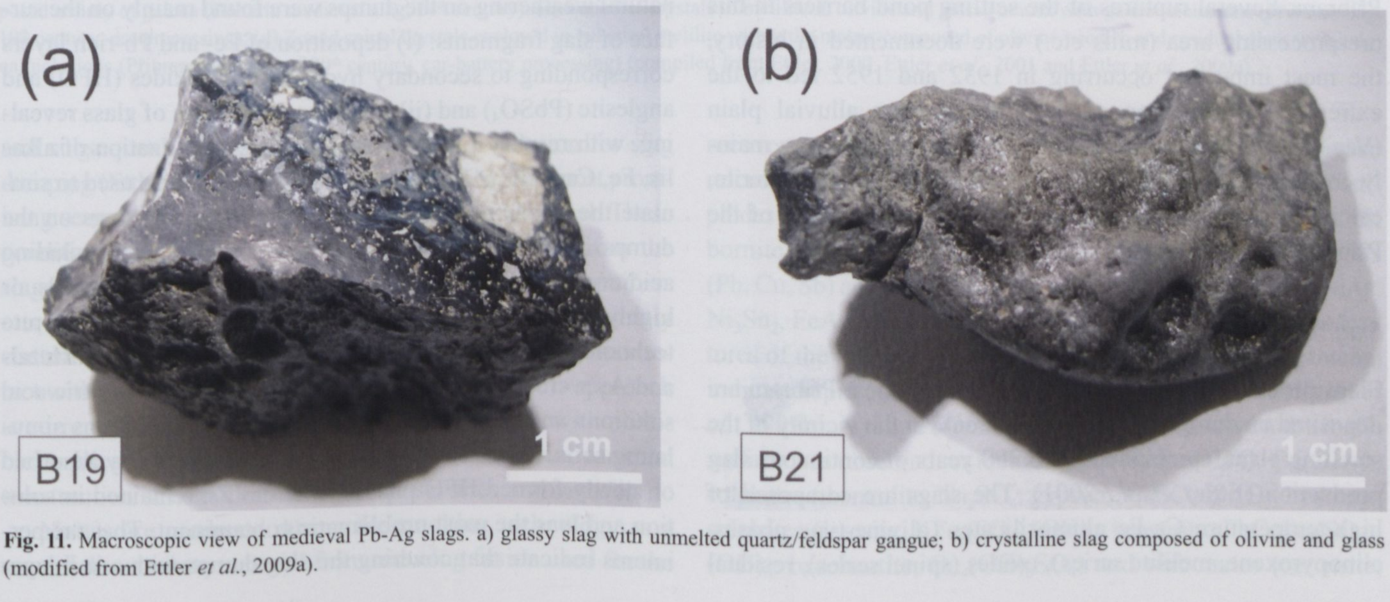



**Fig. 11.** Macroscopic view of medieval Pb-Ag slags. a) glassy slag with unmelted quartz/feldspar gangue; b) crystalline slag composed of olivine and glass (modified from Ettler *et al.*, 2009a).

(Pb, Ag, Sb etc.; Ettler *et al.*, 2001). Silicate slag floated on the surface of the sulphide matte and concentrated the oxide components of the silicate gangue and additives. Slag also contained metal-rich droplets unable to decant in time during the smelting process. The slag was dumped in the vicinity of the smelter (currently the two dumps contain approximately 1.8 millions of tons of slags); mattes, corresponding to sulphide-rich waste materials, were partly recycled for recovery of Cu in Cu-smelters in Slovakia and metals were refined directly in the smelting plant (Vurm, 2001; Ettler *et al.*, 2001).

Since 1972, the smelter has operated as a secondary metallurgical plant, producing Pb from scrap materials, mainly used car batteries. Prior to fusion, the car batteries are crushed and separated from the residual sulphuric acid, which is subsequently treated. Together with the plastic casings of the batteries, Pb-bearing material is mixed with coke (reducing agent and combustible), recycled silica slag (Si source), lime (Ca source) and iron scrap (Fe source). The smelting process is analogous to the ore processing. A modern and environment-friendly processing technology for used car batteries was commenced in 1998 in co-operation with the VARTA company (Ettler *et al.*, 2005a).

Currently, the smelter (called Kovohutě Příbram, a.s., www.kovopb.cz) is one of the most important factories in Central Europe processing electronic waste for the recovery of rare elements (Ag, Au, platinum-group-elements [PGE]). The smelter produces numerous products based on Pb alloys, such as metal plates, solders and ammunition. The smelter has recently received numerous certificates for environment-friendly technologies and activities in remediation of contaminated areas.

## 3.2 Waste materials

### *Mine dumps*

The old mine dumps and tailings related to ore processing are located in the close vicinity of shafts at Březové Hory, Příbram. Several ruptures of the settling pond barriers in this ore-processing area (mills etc.) were documented in history, the most important occurring in 1932 and 1952 led to the extreme contamination of the Litavka river alluvial plain (Vaněk *et al.*, 2008; Žák *et al.*, 2009). The mine dumps, mainly composed of gangue minerals (siderite, dolomite–ankerite, calcite, quartz) are currently accessible in the vicinity of the Příbram Mining Museum at Březové Hory.

### *Slag/matte dumps*

Slags produced by the lead smelter in Lhota near Příbram are deposited on dumps (1.8 millions of tons) in the vicinity of the smelting plant, corresponding to 200 years of continuous slag production (Ettler *et al.*, 2001). The slags are composed of high-temperature Ca-Fe alumosilicates (olivine-type phases, clinopyroxene, melilite series), oxides (spinel series), residual

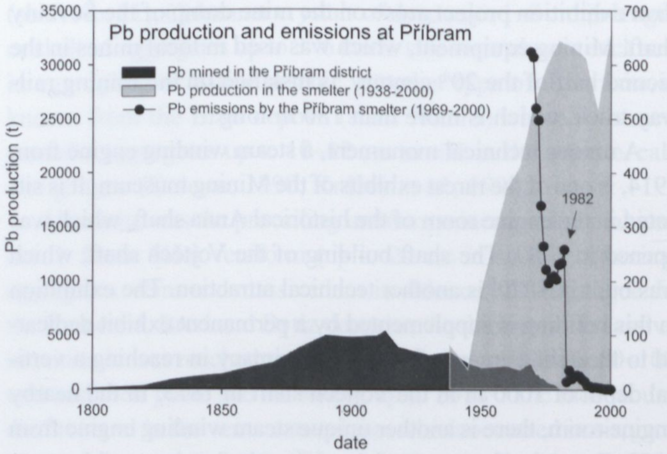



**Fig. 12.** Lead production in the Příbram mining district and in the smelter over the period of last 200 years and recent Pb emissions from the smelter (according to Mihaljevič *et al.*, 2006).

glass and minor sulphides, metals and intermetallic compounds (Ettler *et al.*, 2001; Ettler *et al.*, 2002; Ettler *et al.*, 2003a). Silicates and oxides generally have crystal shapes corresponding to rapid crystallization (quenching), with skeletal or herringbone structures or dendrites (Ettler *et al.*, 2001) (Fig. 13). Sulphides, metals and intermetallic compounds are generally present in small droplets (< 5 µm in size) trapped within the silicate matrix or as larger inclusions (up to 300 µm) composed of phases similar to those found in mattes (Ettler, 2000; see below). The slags are enriched in metals and metalloids, with higher concentrations in slags resulting from ore processing (up to 2.3 wt% Pb, up to 5.8 wt% Zn, up to 300 mg/kg As). In contrast, significantly lower concentrations of these toxic elements were found in modern slags resulting from car-battery processing (0.8 wt% Pb, 0.2 wt% Zn, up to 125 mg/kg As) (Ettler *et al.*, 2003a). Zinc massively substitutes Fe in silicates and oxides (up to 19.9 wt% ZnO in spinel structures and up to 10.5 wt% ZnO in melilite), whereas Pb behaves as an "incompatible element" and is concentrated in residual glass (up to 3.72 wt% PbO; Ettler *et al.*, 2001). The features attributed to natural weathering on the dumps were found mainly on the surface of slag fragments: (i) deposition of Fe- and Pb-rich layers corresponding to secondary hydrous ferric oxides (HFO) and anglesite ($PbSO_4$) and (ii) selective dissolution of glass revealing, with respect to fresh slag glass, the mobilization of alkalis, Fe, Ca and Zn. Laboratory leaching tests were used to simulate the conditions of long-term weathering of slags on the dumps or in the conditions of their potential use (including acidic environments with organic acids simulating soils or highly alkaline conditions specific for application in concrete technologies; Ettler *et al.*, 2002; Ettler *et al.*, 2003a). Metals and As were released more intensely from slags in citric acid solutions and high-molecular-weight organic solutions simulating soils. Released Pb, Cu and As were efficiently adsorbed on newly formed HFO phases, whereas Zn remained in solution and was the most problematic contaminant. These experiments indicate that covering the slag dumps with a soil layer

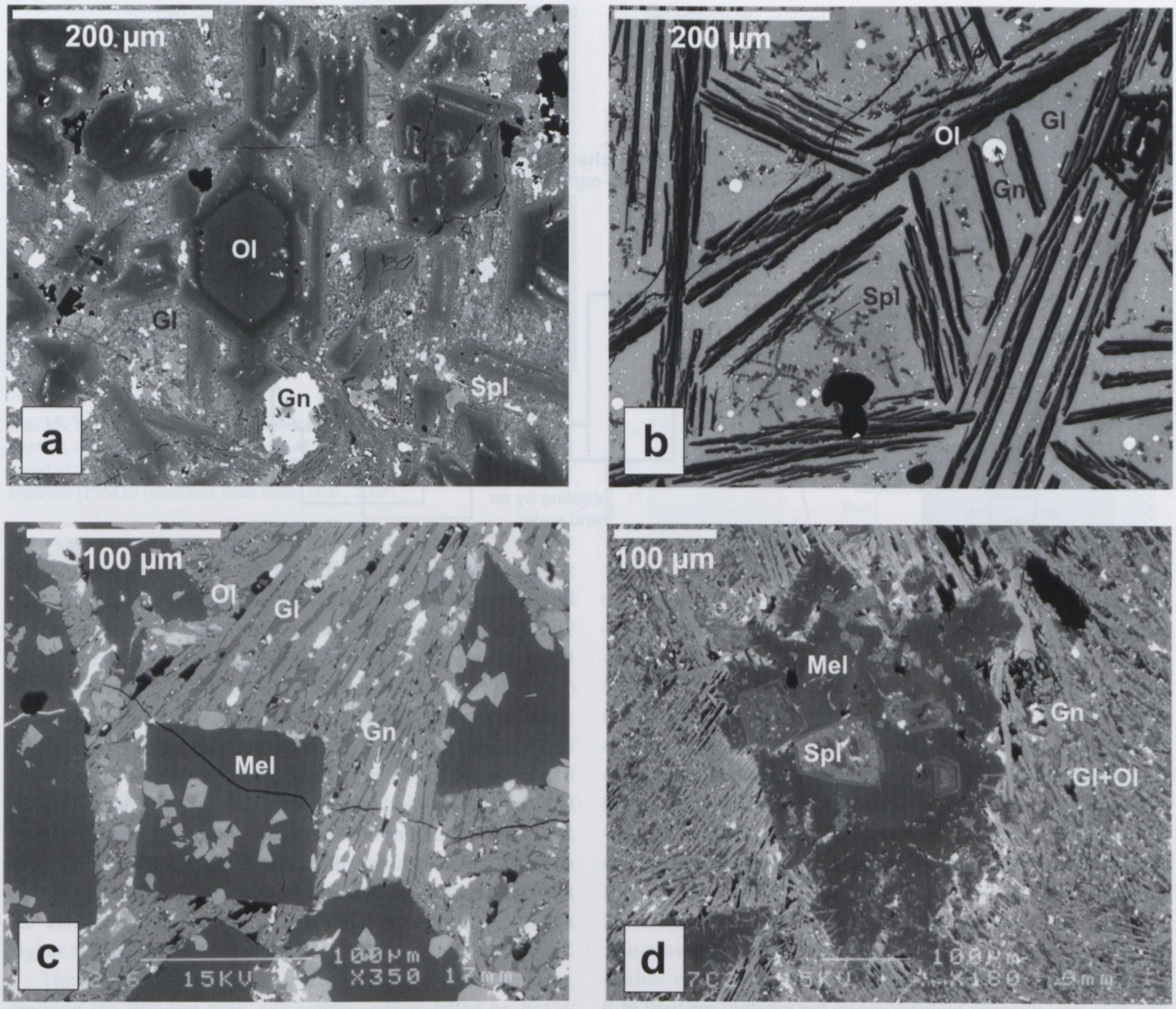
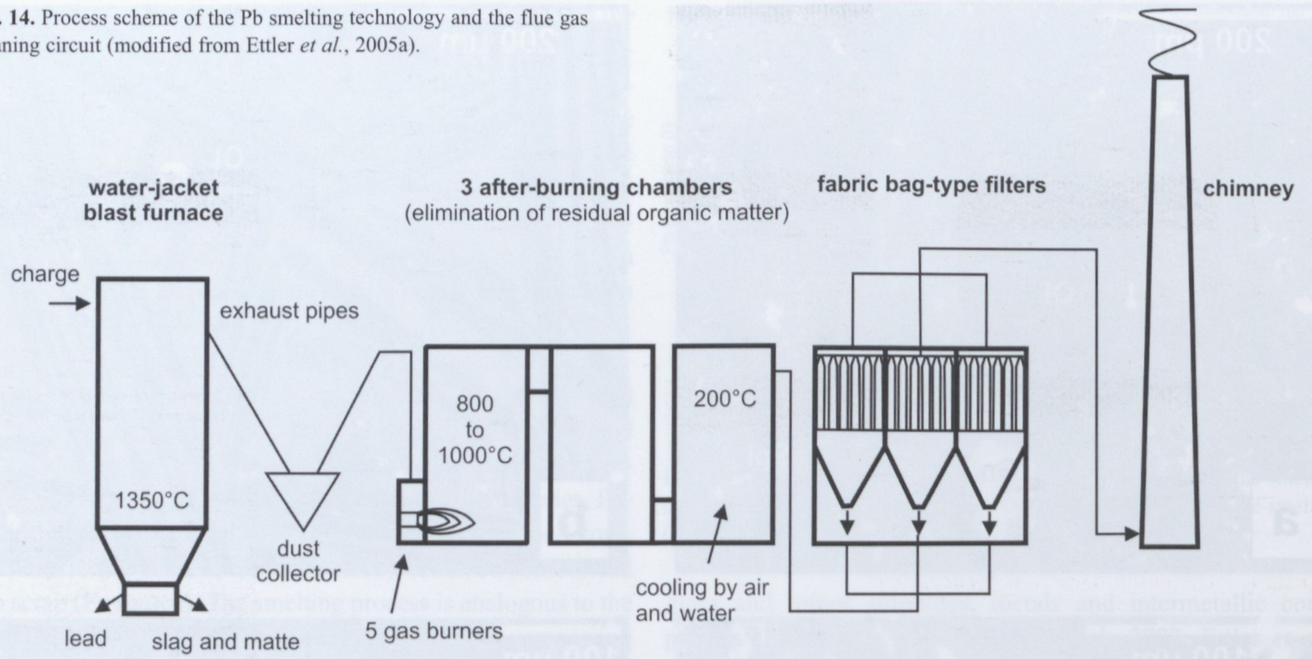



**Fig. 13.** Scanning electron micrographs of silicate phases of the Bohutín medieval slags and more recent slags from the Pb smelter in Lhota near Příbram (back-scattered electron images). (a) Large skeletal crystals of olivine and small spinel crystals within the matrix composed of interstitial glass and galena inclusions (Bohutín medieval slag, 14th century); (b) Large dendritic needles of olivine and small dendrites of spinel in a glass matrix containing metallic droplets composed mainly of galena (Bohutín medieval slag, 14th century); (c) Euhedral crystals of melilite in olivine and glassy matrix with galena inclusions (Příbram slag, 19th century, ore processing); (d) Zoned spinel crystals enclosed in euhedral melilite within the matrix composed of olivine needles and residual glass with galena inclusions (Příbram slag, end of 20th century, car-battery processing) (compiled from Ettler, 2000, Ettler *et al.*, 2001 and Ettler *et al.*, 2009a).

and subsequent re-vegetation is not the best solution for slag dumping (Ettler *et al.*, 2004; Ettler *et al.*, 2005b). The most promising seems to be a "free-air" scenario for slag disposal. These conditions ensure the oxidation of the released Fe from the slags and formation of HFO, which are able to adsorb numerous released contaminants. In addition, Pb can be efficiently controlled by precipitation of anglesite or cerussite (if in contact with atmospheric $CO_2$; Ettler *et al.*, 2003a). This approach is currently employed at the Příbram smelter site, with possible application of new slags as granulated material for road construction at hazardous waste disposal sites and landfills.

Mattes are produced during the smelting technology as a second direct waste material from reducing fusion used for the recovery of sulphur from the furnace charge. Electron-probe microanalysis (EPMA) revealed the presence of various sulphides (galena, PbS; wurtzite/sphalerite, ZnS; pyrrhotite, $Fe_{1-x}S$; bornite, $Cu_5FeS_4$; digenite, $Cu_{9+x}S_5$; cubanite, $CuFe_2S_3$), metals (Pb, Cu, Sb) and complex intermetallic compounds (NiSb, NiAs, $Ni_3Sn_2$, $FeAs_2$, $Fe_2As$, $Cu_5As_2$; Ettler & Johan, 2003). The textures of the phases (skeletal crystals, myrmekitic intergrowths) indicate rapid cooling of the sulphide-metallic melt (Ettler *et al.*, 2009b). A range of natural alteration products on the matte surface was observed: oxides and hydroxides (HFO, $Cu(OH)_2$), sulphates (thenardite, $Na_2SO_4$; gypsum, $CaSO_4{\cdot}2H_2O$), hydroxysulphates (jarosite, $KFe_3(SO_4)_2(OH)_6$; beaverite, $PbCuFe_2(SO_4)_2(OH)_6$; brochantite, $Cu_4(OH)_6SO_4$) and carbonates (cerussite,

**Fig. 14.** Process scheme of the Pb smelting technology and the flue gas cleaning circuit (modified from Ettler *et al.*, 2005a).




$PbCO_3$; malachite, $Cu_2(OH)_2CO_3$; $NaOH{\cdot}2PbCO_3$). The large stability range of the newly formed phases confirms the substantial variety of Eh-pH conditions of natural matte weathering. For example, jarosite is stable at pH < 3, but some hydroxides and carbonates are typically formed under neutral to alkaline conditions. Consequently, it is difficult to determine the best dumping conditions for mattes and these materials should be either dumped in controlled waste-disposal sites or used in contaminated environments (such as the current practice of matte application in road construction at U-containing tailing ponds).

*Fly ash*

The flue-gas cleaning technology in the smelter consists of a dust collector, three after-burning chambers, three parallel bag-type filters and a chimney (Fig. 14). Silicates (quartz, muscovite), anglesite and Pb-rich glass are the most abundant phases in the coarse-grained dust collected in a collector located directly after the exhaust of the blast furnace (Ettler *et al.*, 2005). The presence of anglesite and laurionite [Pb(OH)Cl] was observed in the sintered residue from after-burning chambers (800–1000 °C). In contrast, low-temperature Pb-bearing phases, such as $KCl{\cdot}2PbCl_2$ and caracolite [$Na_3Pb_2(SO_4)_3Cl$], were detected in the major air-pollution-control (APC) residues from bag-type filters (Ettler *et al.*, 2005a). These waste materials are highly soluble and can be ranged within the hazardous materials as revealed the laboratory leaching tests (Ettler *et al.*, 2005a; Ettler *et al.*, 2005c; Ettler *et al.*, 2008; Vítková *et al.*, 2009) (Fig. 15). The APC residues from bag-type filters are collected and sintered in a rotary furnace at 300-500 °C to recover Pb.

The Pb emissions from the Příbram smelter decreased from 624 ton of Pb per year in 1969 to 1.2 ton of Pb per year in 1999 as a result of improved efficiency of the flue gas treatment technology, where the efficiency of the bag-type filter is 99.85%. The amount of emitted dust is <2 mg/m$^3$ and that of $SO_2$ ranges from 50 to 100 mg/m$^3$ (Ettler *et al.*, 2005a).

The historical emissions of metals from the smelter were monitored using geochemical archives: $^{210}$Pb-dated cores from a peat deposit located approximately 12 km WNW of the smelter stack in the Brdy Hills area (Mihaljevič *et al.*, 2006; Ettler *et al.*, 2008b) and spruce (*Picea abies* tree-rings) in forested areas at various distances of the smelter (Mihaljevič *et al.*, 2008). The peak of Pb deposition was observed between the 1960s and 1980s (between 145 and 320 mg/m$^2$/year), corresponding to highest smelter emissions (Mihaljevič *et al.*, 2006; Ettler *et al.*, 2008b, Mihaljevič *et al.*, 2008).

## 3.3 Soil and watershed contamination

The historical emissions from smelting activities in the Příbram area resulted in extensive contamination of soils, especially the upper soil horizons. Rieuwerts *et al.* (1999) and Ettler *et al.* (2007) found extremely high concentrations of metals in this area: up to 58,500 mg Pb/kg, 21,900 mg Zn/kg, 2,440 mg Cu/kg, 96 mg Cd/kg and up to 6.5 mg Hg/kg. Nevertheless, large differences in the degree of contamination were observed and were related in particular to the distance from the smelter stack and the prevailing wind direction (from NW to SE). Whereas forest soils were found to be the richest in metals due to higher interception of smelter emissions by tree canopies (a horizon with 35,400 mg Pb/kg), agricultural soils contain only up to 1233 mg Pb/kg, homogeneously distributed in the upper 20-cm layer, corresponding to the depth of cultivation (ploughing) (Ettler *et al.*, 2005d). Sequential extraction analysis showed that Pb can be significantly more mobile in forest soils, being mainly bound by sorption to exchangeable positions on organic

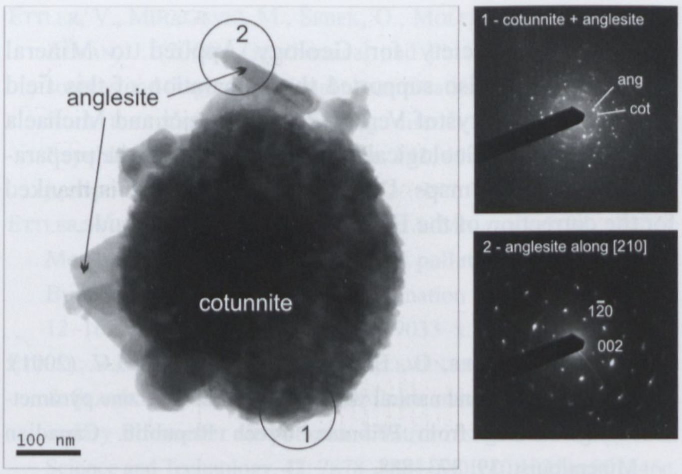



**Fig. 15.** Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns of the leached fly ash particles composed of newly formed spherical cotunnite ($PbCl_2$) associated with crystals of anglesite ($PbSO_4$) (modified from Ettler *et al.*, 2008).

matter (Fig. 16). In contrast, Pb in tilled soils is mainly bound to the reducible fraction, nominally corresponding to Fe and Mn oxyhydroxides (Ettler *et al.*, 2005d). The Pb isotopic study of Pb sources and mobility in the Příbram soils showed that Pb resulting from car-battery processing (in operation since 1972) is more mobile that Pb derived from ore processing (Ettler *et al.*, 2004b). This observation is related to the higher reactivity of secondary Pb smelter emissions (corresponding to fly ash released by the smelter stack during car-battery processing) because of the presence of extremely soluble Pb chlorides (Ettler *et al.*, 2005d). Recent studies of pH-dependent leaching of metals indicated that, under acidic conditions (forest soil pH of 3.5), the smelter APC residues exhibit 2-3 orders of magnitude higher release of metals and metalloids (Vítková *et al.*, 2009).

The alluvial plain and the watershed of the Litavka River, draining the Příbram area, are highly contaminated by heavy metals (Ettler *et al.*, 2006; Vaněk *et al.*, 2005; Vaněk *et al.*, 2008; Žák *et al.*, 2009). A set of 37 stream sediment samples from the Litavka River and Příbramský stream indicated that the highest metal concentrations were found 3–4 km downstream from the main polymetallic mining site at Březové Hory (9800 mg/kg Pb, 26,039 mg/kg Zn, 316 mg/kg Cd and 257 mg/kg Cu) (Ettler *et al.*, 2006). Sequential extractions showed that Pb, Zn and Cd are mainly bound to Fe oxides and hydroxides, which were detected in stream sediments by mineralogical methods, together with the presence of Pb carbonates and litharge (PbO) (Ettler *et al.*, 2006). Furthermore, the isotopic composition of Pb in stream sediments corresponded well to primary Pb smelting (ores have $^{206}Pb/^{207}Pb = 1.16$), while the role of secondary smelting (car battery processing) is negligible (Ettler *et al.*, 2006). During the flood events, the contamination was commonly redistributed within the Litavka River alluvial plain (Vaněk *et al.*, 2005; Vaněk *et al.*, 2008). Up to 7590 mg/kg Pb, 4949 mg/kg Zn, 45 mg/kg Cd and 740 mg/kg As were detected in alluvial soils, mainly in the vicini-

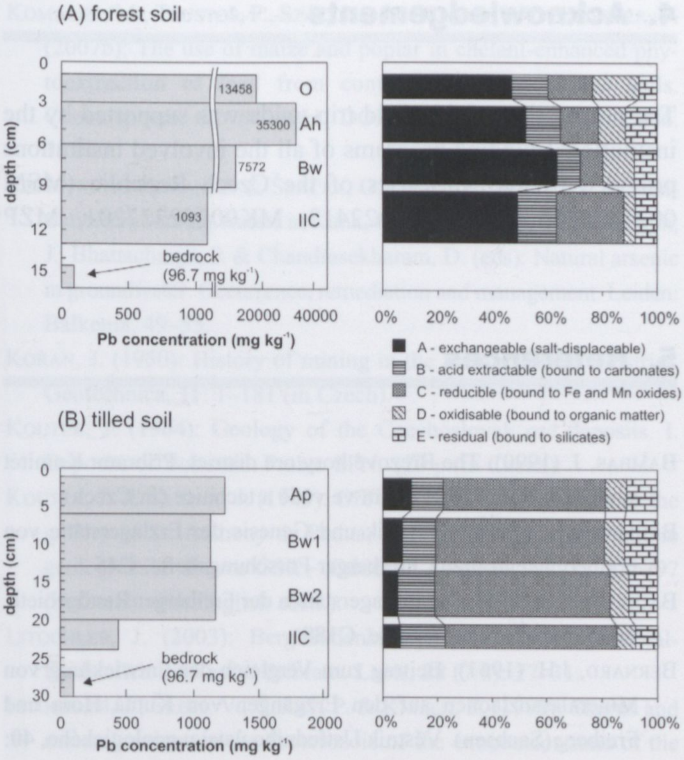



**Fig. 16.** Distribution and speciation of Pb in highly polluted forest and tilled soils in the vicinity of the Příbram smelter (modified from Ettler *et al.*, 2005d).

ty of the Březové Hory mining area (Vaněk *et al.*, 2008). Iron oxides and hydroxides and birnessite ($Na_4Mn_{14}O_{27}\cdot 9H_2O$) were detected by SEM/EDS and XRD as the most important carriers for metals and metalloids in the contaminated alluvial soils (Vaněk *et al.*, 2008). The floodplain close to Trhové Dušníky (5 km N of Příbram) is composed of a 1–1.7-m thick fine-grained and highly contaminated soil/sediment layer. The studies of fluxes of metals during the flood events indicated that they are transported mostly in the form of suspended particulate matter (SPM) (*e.g.*, more than 99% for Pb). During a single snowmelt-related minor flood event between March 25 and 29, 2006 (peak flow 36.6 $m^3/s$), the river transported 2400 tons of SPM during 4 days, containing 74 kg of Cd, 2954 kg of Pb and 5811 kg of Zn (Žák *et al.*, 2009).

During recent years, numerous phytoremediation and phytoextraction studies were performed on mining-affected alluvial soils (Tlustoš *et al.*, 2007) and smelting-affected agricultural soils (Komárek *et al.*, 2007a; Komárek *et al.*, 2007b; Komárek *et al.*, 2008). Tlustoš *et al.* (2007) found efficient phytoextraction of Cd and Zn by willow plants (*Salix* sp.) grown on the contaminated Litavka River alluvial plain. Cadmium was efficiently translocated to maize (*Zea mays*), when phytoextraction was enhanced by addition of chloride salts to smelter-polluted agricultural soils (Komárek *et al.*, 2007a). Up to 60% of Pb from contaminated soil was removed by enhanced phytoextraction using organic chelants (EDTA, EDDS) by poplar (*Populus* sp.) and maize (*Zea mays*) (Komárek *et al.*, 2007b; Komárek *et al.*, 2008).

## 4. Acknowledgements

The preparation of this field trip guide was supported by the institutional funding programs of all the involved institutions provided by the Ministries of the Czech Republic (MSM 0021620855, MSM0021622412, MK00002327201, MZP 0002579801). Society for Geology Applied to Mineral Deposits (SGA) also supported the preparation of this field trip guide. Drs. Kryštof Verner, Zuzana Krejčí and Michaela Zemková (Czech Geological Survey) helped with the preparation of geological maps. Dr. Madeleine Štulíková is thanked for the correction of the English in this field trip guide.

## 5. References

Bambas, J. (1990): The Březové hory ore district. Příbram: Komitét sympozia Hornická Příbram ve vědě a technice (in Czech).

Baumann, L. (1958): Tektonik und Genesis der Erzlagerstätte von Freiberg (Zentralteil). Freiberger Forschungshefte, **C46**.

Baumann, L. (1965): Die Erzlagerstätten der Freiberger Randgebiete. Freiberger Forschungshefte, **C188**.

Bernard, J.H. (1961): Beitrag zum Vergleich der Entwicklung von Mineralassoziaonen auf den Erzgängen von Kutná Hora und Freiberg (Sachsen). Věstník Ústředního ústavu geologického, **40**: 289–291.

Bernard, J.H. (1967): Kurze Übersicht der isogenetischen erzlagerbildenden Mineralassoziationen hydrothermalen Ursprungs im tschechoslowakischen Teil der Böhmischen Masse. Časopis pro Mineralogii a Geologii,, **12**: 13–20.

Bernard, J. H. (1991): Empirical types of the ore mineralizations in the Bohemian Massif. Praha: Ústřední ústav geologický, 181 p.

Bernard, J. H. (2000): Minerals of the Czech Republic, Praha: Academia, 186 p (in Czech).

Bukovský, A. (1915): Poisonous clay from Kutná Hora. Dvanáctá výroční zpráva c. k. státní reálky v Nymburce za školní rok 1914–1915, 3–4 (in Czech).

Čech, F., Jansa, J. & Novák, F. (1976): Kaňkite, $FeAsO_4 \cdot 3H_2O$, a new mineral. Neues Jahrbuch für Mineralogie – Monatshefte, **9**: 426–436.

Čech, F., Jansa, J. & Novák, F. (1978): Zýkaite, $Fe^{3+}{}_4(AsO_4)_3(SO_4)(OH) \cdot 15H_2O$, a new mineral. Neues Jahrbuch für Mineralogie – Monatshefte, **3**: 134–144.

Drahota, P. & Filippi, M. (2009): Secondary arsenic minerals in the environment: A review. Environmental International, **35**: 1243–1255. DOI: 10.1016/j.envint.2009.07.004.

Ettler, V. (2000): Etude du potentiel polluant de rejets anciens et actuels de la métallurgie du plomb dans le district de Příbram (République tchèque). PhD thesis, University of Orléans, France.

Ettler, V. & Johan, Z. (2003): Mineralogy of metaloid phases in sulphide mattes from primary lead smelting. Comptes Rendus Geoscience, **335**: 1005–1012. DOI: 10.1016/j.crte.2003.09.005.

Ettler, V., Johan, Z., Touray, J.C. & Jelínek, E. (2000): Zinc partitioning between glass and silicate phases in historical and modern lead-zinc metallurgical slags from the Příbram district, Czech Republic. Comptes Rendus de l'Académie des Sciences, Paris, série II, **331**: 245–250.

Ettler, V., Legendre, O., Bodénan, F. & Touray, J.C. (2001): Primary phases and natural weathering of old lead-zinc pyrometallurgical slag from Příbram, Czech Republic. Canadian Mineralogist, **39**: 873–888.

Ettler, V., Mihaljevič, M., Touray, J.C. & Piantone, P. (2002): Leaching of polished sections: an integrated approach for studying the liberation of heavy metals from lead-zinc metallurgical slags. Bulletin de la Société Géologique de France, **173**: 161–169.

Ettler, V., Piantone, P. & Touray, J.C. (2003a): Mineralogical control on inorganic contaminant mobility in leachate from lead-zinc metallurgical slag: experimental approach and long-term assessment. Mineralogical Magazine, **67**: 1269–1283. DOI: 10.1180/0026461036760164.

Ettler, V., Johan, Z. & Hradil, D. (2003b): Natural alteration products of sulphide mattes from primary lead smelting. Comptes Rendus Geoscience, **335**: 1013–1020. DOI: 10.1016/j.crte. 2003.09.006.

Ettler, V., Komárková, M., Jehlička, J., Coufal, P., Hradil, D., Machovič, V. & Delorme, F. (2004a): Leaching of lead metallurgical slag in citric solutions–implications for disposal and weathering in soil environments. Chemosphere, **57**: 567–677. DOI: 10.1016/j.chemosphere.2004.07.022.

Ettler, V., Mihaljevič, M., Komárek, M. (2004b): ICP-MS measurements of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution. Analytical and Bioanalytical Chemistry, **378**: 311–317. DOI: 10.1007/s00216–003–2229–y.

Ettler, V., Johan, Z., Baronnet, A., Jankovský, F., Gilles, C., Mihaljevič, M., Šebek, O., Strnad, L. & Bezdička, P. (2005a): Mineralogy of air-pollution-control residues from a secondary lead smelter: Environmental implications. Environmental Science and Technology, **39**: 9309–9316. DOI: 10.1021/es0509174.

Ettler, V., Jehlička, J., Mašek, V. & Hruška, J. (2005b): The leaching behaviour of lead metallurgical slag in high-molecular-weight (HMW) organic solutions. Mineralogical Magazine, **69**: 737–747. DOI: 10.1180/0026461056950284.

Ettler, V., Mihaljevič, M., Šebek, O. & Strnad, L. (2005c): Leaching of APC residues from secondary Pb metallurgy using single extraction tests: the mineralogical and the geochemical approach. Journal of Hazardous Materials, **B121**: 149–157. DOI: 10.1016/j.jhazmat.2005.02.001.

Ettler, V., Vaněk, A., Mihaljevič, M. & Bezdička, P. (2005d): Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. Chemosphere, **58**: 1449–1459. DOI: 10.1016/j.chemosphere.2004.09.084.

Ettler, V., Mihaljevič, M., Šebek, O., Molek, M., Grygar, T. & Zeman, J. (2006): Geochemical and Pb isotopic evidence for sources and dispersal of metal contamination in stream sediments from the mining and smelting district of Příbram, Czech Republic. Environmental Pollution, **142**: 409–417. DOI: 10.1016/j.envpol.2005.10.024.

Ettler, V., Rohovec, J., Navrátil, T. & Mihaljevič, M. (2007): Mercury distribution in soil profiles polluted by lead smelting. Bulletin of Environmental Contamination and Toxicology, **78**: 12–16. DOI: 10.1007/s00128–007–9033–x.

Ettler, V., Šebek, O., Grygar, T., Klementová, M., Bezdička, P. & Slavíková, H. (2008a): Controls on metal leaching from secondary Pb smelter air-pollution-control residues Environmental Science and Technology, **42**: 7878–7884. DOI: 10.1021/es801246c.

Ettler, V., Navrátil, T., Mihaljevič, M., Rohovec, J., Zuna, M., Šebek, O., Strnad, L. & Hojdová, M. (2008b): Mercury deposition/accumulation rates in the vicinity of a lead smelter as recorded by a peat deposit. Atmospheric Environment, **42**: 5968–5977. DOI: 10.1016/j.atmosenv.2008.03.047.

Ettler, V., Červinka, R. & Johan, Z. (2009a): Mineralogy of medieval slags from lead and silver smelting (Bohutín, Příbram district, Czech Republic): Towards estimation of historical smelting conditions. Archaeometry, **51**: 987–1007. DOI: 10.1111/j.1475–4754.2008.00455.x.

Ettler, V., Johan, Z., Bezdička, P., Drábek, M., Šebek, O. (2009b): Crystallization sequences in mattes from primary lead smelting. European Journal of Mineralogy, **21**: 873–854. DOI: 10.1127/0935–1221/2009/0021–1942.

Hak J., Kvaček, M. & Watkinson, D.H. (1983): Indium content of sphalerite from Turkaňk zone in the Kutná Hora base metal deposit (Bohemia). Časopis pro Mineralogii a Geologii, **28** (1): 65–69.

Holub, M., Hoffman, V., Mikuš, M. & Trdlička, Z. (1982): Polymetallic mineralization of Kutná Hora ore district. Sborník Geologických Věd – Ložisková Geologie, Mineralogie, **23**: 69–123 (in Czech).

Knížek, F. & Litochleb, J. (2005): Calcite druse cavities with whewellite on the Bytíz uranium deposit (the Příbram uranium-polymetallic district, central Bohemia). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **13**: 73–77 (in Czech)Knížek, F, Litochleb, J. & Šrein, V. (1990): Dyscrasite and allargentum from the Háje vein bundle of the Příbram uranium deposit. Věstník Ústředního ústavu geologického, **65**: 321–328.

Kolesar, P. (1990): Dyskrasit-Kristalle aus dem Bergbaurevier Pribram in der Tschechoslowakei. Lapis, **18** (9): 19–26.

Komárek, M., Tlustoš, P., Száková, J. & Chrastný, V. (2008): The use of poplar during a two-year induced phytoextraction of metals from contaminated agricultural soils. Environmental Pollution, **151**: 27–38. DOI:10.1016/j.envpol.2007.03.010.

Komárek, M., Tlustoš, P., Száková, J. & Chrastný, V. (2007a): The role of chloride salts in chemically enhanced phytoextraction of heavy metals from a contaminated agricultural soil. Bulletin of Environmental Contamination and Toxicology, **78**: 166–170. DOI: 10.1007/s00128–007–9029–6.

Komárek, M., Tlustoš, P., Száková, J., Chrastný, V. & Ettler, V. (2007b): The use of maize and poplar in chelant-enhanced phytoextraction of lead from contaminated agricultural soils. Chemosphere, **67**: 640–651. DOI:10.1016/j.chemosphere.2006.11.010.

Kopřiva, A., Zeman, J. & Šráček, O. (2005): High arsenic concentrations in mining waters at Kaňk, Czech Republic. In Bundschuh, J., Bhattacharya, P. & Chandrasekharam, D. (eds): Natural arsenic in groundwater: Occurrence, remediation and management. Leiden: Balkema, 49–55.

Kořan, J. (1950): History of mining in the Kutná Hora ore district. Geotechnica, **11**: 1–181 (in Czech).

Koutek, J. (1964): Geology of the Czechoslovak ore deposits. I. Deposits of Bohemia. Praha: SPN. 120 p (in Czech).

Koutek, J. & Kutina, J. (1949): Ore veins and their minerals in the gallery of St. Anthony de Padua, Kutná Hora. Sborník Státního geologického ústavu ČSR – Oddělení geologie, **16(2)**: 783–797 (in Czech with English abstr.).

Litochleb, J. (2003): Bergbaudenkmäler und aktuelle Mineralfundstellen im Revier Príbram. Lapis, **28** (7/8): 27–31.

Litochleb, J., Šrein, V., Černý, P. & Knížek, F. (1998): Skarns and mineralizations in the Proterozoic of the exocontact zone of the Central Bohemian pluton in the area of the uranium deposit Příbram. Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **6**: 113–119 (in Czech).

Litochleb, J., Šrein, V., Jindra, J., Sejkora, J. & Šreinová, B. (2000a): Mineralogy of the complex Pb-Zn-Ni-Sb-U-Ag-Hg mineralization from the Řimbabská severozápadní vein, deposit Bohutín near Příbram. Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **8**: 145–156 (in Czech).

Litochleb, J., Černý, P., Lantora, M., Šrein, V. & Sejkora, J. (2000b): The underground gas reservoir at Háje near Příbram (Central Bohemia) – knowledge from mineralogical research. Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **8**: 68–74 (in Czech).

Litochleb, J., Sejkora, J. & Šrein, V. (2002): Mineralogy of silver mineralization from Brod near Příbram (uranium–polymetallic ore district). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **10**: 221–234 (in Czech).

Litochleb, J., Černý, P., Litochlebová, E., Sejkora, J. & Šreinová, B. (2003): The deposits and occurrences of mineral raw materials in the Střední Brdy Mts. and the Brdy piedmont area (Central Bohemia). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **11**: 57–86 (in Czech).

Litochleb, J., Sejkora, J. & Šrein, V. (2004): Selenides from the Bytíz occurrence (Příbram uranium–polymetallic ore district). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **12**: 113–123 (in Czech).

Litochleb, J., Novák, M., Sejkora, J. & Vlašímský, P. (2005): Lithium pegmatite with lepidolite and topaz from Příbram – Skalka (shaft No. 20), central Bohemia (Czech Republic). Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **13**: 140–149 (in Czech).

LOSERT, J. (1968): Tourmaline-cassiterite formations at Kutná Hora ore district. Věstník Ústředního ústavu geologického, **43** (5): 349–357 (in Czech).

MALEC, J. (1997): Historical mine maps from the Kutná Hora ore district. Minerál, **6**: 406–413 (in Czech).

MANASSE, A. & MELLINI, M. (2002): Archaeometallurgic slags from Kutná Hora. Neues Jahrbuch für Mineralogie – Monatshefte, **8**: 369–384. DOI: 10.1127/0028–3649/2002/2002–0369.

MIHALJEVIČ, M., ZUNA, M., ETTLER, V., ŠEBEK, O., STRNAD, L. & GOLIÁŠ, V. (2006): Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic). Science of the Total Environment, **372**: 334–344. DOI: 10.1016/j.scitotenv.2006.09.019.

MIHALJEVIČ, M., ZUNA, M., ETTLER, V., CHRASTNÝ, V., ŠEBEK, O., STRNAD, L. & KINCL, T. (2008): A comparison of tree rings and peat deposit geochemical archives in the vicinity of a lead smelter. Water, Air, and Soil Pollution, **188**: 311–321. DOI: 10.1007/s11270–007–9546–2.

NOVÁK, F., POVONDRA, P. & VTĚLENSKÝ, J. (1967): Bukovskýite, $Fe^{3+}_2(AsO_4)_3(SO_4)(OH)\cdot 7H_2O$, from Kaňk, near Kutná Hora – a new mineral. Acta Universitatis Carolinae – Geologica, **4**: 297–325.

ONDRUŠ, P., SKÁLA, R., VITI, C., VESELOVSKÝ, F., NOVÁK, F. & JANSA, J. (1999): Parascorodite, $FeAsO_4\cdot 2H_2O$ – a new mineral from Kaňk near Kutná Hora, Czech Republic. American Mineralogist, **84**: 1439–1444.

PAULIŠ, P. (1998): Minerals of the Kutná Hora ore district. Kutná Hora: Kuttna, 48 p (in Czech).

RIEUWERTS, J.S., FARAGO, M., CIKRT, M. & BENCKO, V. (1999): Heavy metal concentrations in and around households near a secondary lead smelter. Environmental Monitoring and Assessment **58**: 317–335.

RŮŽIČKA, J. (1986): Minerals of the Příbram uranium deposit. Příbram: VZUP Kamenná (in Czech).

SEJKORA, J. & LITOCHLEB, J. (2003a): Die primäre Mineralisation der Príbramer Erzzone und ihre interessantesten Mineralien. Lapis, **28** (7/8): 32–59.

SEJKORA, J. & LITOCHLEB, J. (2003b): Sekundärmineralien aus der Príbramer Erzzone. Lapis, **28 (7/8)**: 60–70.

SEJKORA, J., LITOCHLEB, J. & ZEMEK, V. (2002a): Contribution to the knowledge of the chemical composition of ore minerals from the southern part of the Kutná Hora ore district. Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **10**: 283–289 (in Czech).

SEJKORA, J., VELEBIL, D. & LITOCHLEB, J. (2002b): A significant mineralogical locality – St. Anthony of Padua Gallery at Poličany, near Kutná Hora. Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **10**: 171–178 (in Czech).

ŠKÁCHA, P. & PLÁŠIL, J. (2002): Minerals of the Březové Hory ore district. Bulletin mineralogicko-petrologického oddělení Národního muzea v Praze, **10**: 43–77 (in Czech).

ŠKÁCHA, P., GOLIÁŠ, V., SEJKORA, J., PLÁŠIL, J., STRNAD, L., ŠKODA, R. & JEŽEK, J., (2009): Hydrothermal uranium – base metal mineralization of the Jánská vein, Březové Hory, Příbram, Czech Republic: lead isotopes and chemical dating of uraninite. Journal of Geosciences, **54(1)**: 1–13.

TLUSTOŠ, P., SZÁKOVÁ, J., VYSLOUŽILOVÁ, M., PAVLÍKOVÁ, D., WEGER, J. & JAVORSKÁ, H. (2007): Variation in the uptake of arsenic, cadmium, lead, and zinc by different species of willows Salix spp. grown in contaminated soils. Central European Journal of Biology, **2**: 254–275. DOI: 10.2478/s11535–007–0012–3.

TRDLIČKA, Z. (1963): Secondary minerals from medieval slags in Kutná Hora. Sborník Oblastního muzea v Kutné Hoře, řada geologicko-báňská, **3**: 3–10 (in Czech).

TRDLIČKA, Z. (1964): Native copper from medieval slags in Kutná Hora. Sborník Oblastního muzea v Kutné Hoře, řada geologicko-báňská, **4**: 7–14 (in Czech).

TVRDÝ, J. (2003): Silber, Buntmetalle und Uran: Die Geschichte des Bergaureviers Pribram. Lapis, **28** (7/8): 13–22.

VANĚK, A., ETTLER, V., GRYGAR, T., BORŮVKA, L., ŠEBEK, O. & DRÁBEK, O. (2008): Combined chemical and mineralogical evidence for heavy metal binding in mining- and smelting-affected alluvial soils. Pedosphere, **18**: 464–478. DOI: 10.1016/S1002–0160(08)60037–5.

VELFL, J. (ed.) (2007): Time tracking. Mining activities in Central Bohemia. Praha: Středočeský kraj, 135 p.

VELFL, J. (2008): The sights of Příbram in pictures. Příbram: Město Příbram, 200 p.

VÍTKOVÁ, M., ETTLER, V., ŠEBEK, O., MIHALJEVIČ, M., GRYGAR, T. & ROHOVEC, J. (2009): The pH-dependent leaching of inorganic contaminants from secondary lead smelter fly ash. Journal of Hazardous Materials, **167**: 427–433. DOI: 10.1016/j.hazmat.2008.12.136

VURM, K. (2001): History of the Příbram smelters, 1311–2000. Příbram: Kovohutě Příbram, 200 p (in Czech).

ŽÁK, K., ROHOVEC, J. & NAVRÁTIL, T. (2009): Fluxes of heavy metals from a highly polluted watershed during flood events: a case study of the Litavka river, Czech Republic. Water, Air, and Soil Pollution, **203**: 343–348. DOI: 10.1007/s11270–009–0017–9.

ZEMAN, J. (2008): Long-term trends of mine waters. In Černík, M. *et al.* (eds): Geochemistry and remediation of mine waters. Prague: AQUATEST a.s.: 81–100 (in Czech).

# Appendix – Itinerary for IMA2010 CZ3 Field trip

## Sunday, August 29, 2010 (Day 1)

| | |
|---|---|
| 09:00 | Introduction to the field trip – Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, Prague 2 (GPS: 50°4′8.009″N, 14°25′28.154″E). Other information concerning the study of geology at Charles University is given on the official website: http://www.natur.cuni.cz/geologie. The beginning of the field trip will be devoted to a short, 15-min presentation of the main points, field stops and time schedule by the organizers in one of the lecture halls of Charles University, Albertov 6 building. |
| 09:30–11:00 | Visit to the Mineralogical Collections of Charles University (https://www.natur.cuni.cz/geologie-en/mineralogical-museum/mineralogical-museum?set_language=en) and the Chlupač Museum of Earth's History at Charles University (https://www.natur.cuni.cz/geologie/chlupacovo-muzeum). |
| 11:00–12:00 | Travel to Kutná Hora, lunch, accommodation |
| 14:00 | Geology and mining history of Kutná Hora – the Museum of Silver Mining (GPS: 49°56′51.697″N, 15°15′55.357″E) |
| 17:00 | Free programme – possible visit to St. Barbara (Sv. Barbora) gothic cathedral (GPS: 49°56′41.844″N, 15°15′48.233″E) |

## Monday, August 30, 2010 (Day 2)

| | |
|---|---|
| 09:00 | Visit to the processing plant at Kaňk, mine tailings, acid mine waters (GPS: 49°58′31.966″N, 15°15′48.233″) |
| 11:00 | Mineral collection at the Kaňk dumps (type locality of kaňkite, bukovskýite; GPS: 49°58′40.063″N, 15°16′7.82″E) |
| 12:00 | Lunch at Kutná Hora |
| 13:00 | Mills and old pyrometallurgical plants around the Vrchlice river (collecting of minerals at slag dumps and in the vicinity of the St. Anthony de Padua gallery) (GPS: 49°55′52.193″N, 15°15′25.566″E) |
| 17:00 | Travel to Prague, accommodation and free evening programme |

## Tuesday, August 31, 2010 (Day 3)

| | |
|---|---|
| 09:00 | Departure from Charles University to Příbram |
| 10:30 | Visit to the Příbram smelter and nearby dumps (GPS: 49°42′28.533″N, 13°58′57.971″E) |
| 11:30 | Lunch in the smelter canteen |
| 12:30 | The Příbram museum of mining history, mineralogical collections, mineral collecting on the dumps and visit to the underground galleries (GPS: 49°40′59.864″N, 13°59′11.699″E). |
| 16:30 | Visit to the baroque monastery at Svatá Hora (near Příbram) |
| 18:30 | Arrival in Prague (Charles University) |

# USEFUL NOTES

## INSTRUCTIONS FOR AUTHORS

### General

Acta Mineralogica-Petrographica (AMP) publishes articles (papers longer than 4 printed pages but shorter than 16 pages, including figures and tables), notes (not longer than 4 pages, including figures and tables), and short communications (book reviews, short scientific notices, current research projects, comments on formerly published papers, and necrologies of 1 printed page) dealing with crystallography, mineralogy, ore deposits, petrology, volcanology, geochemistry and other applied topics related to the environment and archaeometry. Articles longer than the given extent can be published only with the prior agreement of the editorial board.

In the form of two subseries, AMP publishes materials of conferences (AMP Abstract Series) and field guides (AMP Field Guide Series), or, occasionally supplement issues related to other scientific events.

The journal accepts papers that represent new and original scientific results, which have not appeared elsewhere before, and are not in press either.

All articles and notes submitted to AMP are reviewed by two referees (short communications will be reviewed only by one referee) and are normally published in the order of acceptance, however, higher priority may be given to Hungarian researches and results coming from the Alpine-Carpathian-Dinaric region. Of course, the editorial board does accept papers dealing with other regions as well, let they be compiled either by Hungarian or foreign authors.

The manuscripts (prepared in harmony of the instructions below) must be submitted to the Editorial Office in triplicate. All pages must carry the author's name, and must be numbered. At this stage (revision), original illustrations and photographs are not required, though, quality copies are needed. It is favourable, if printable manuscripts are sent on disk, as well. In these cases the use of Microsoft Word or any other IBM compatible editing programmes is suggested.

### Language

The language of AMP is English.

### Preparation of the Manuscript

The different parts of the manuscript need to meet the instructions below:

*Title*

The title has to be short and informative. No subtitles if possible. If the main title is too long, an additional shortened title is needed for the running head.

*Author*

The front page has to carry (under the main title) the full name(s) (forename, surname), affiliation(s), current address(es), e-mail address(es) of the author(s).

*Abstract and keywords*

The abstract is required to be brief (max. 250 words), and has to highlight the aims and the results of the article. The abstracts of notes are alike (but max. 120 words). As far as possible, citations have to be avoided.

The abstract has to be followed by 4 to 10 keywords.

*Text and citations*

The format of the manuscripts is required to be: double-spacing (same for the abstract), text only on one side of the page, size 12 Times New Roman fonts. Margin width is 2.5 cm, except the left margin, which has to be 3.5 cm wide. Underlines and highlights ought not be used. Please avoid the use of foot and end notes. Accents of Romanian, Slovakian, Czech, Croatian etc. characters must be marked on the manuscript clearly.

When compiling the paper an Introduction – Geological setting – Materials and Methods – Results – Conlclusions structure is suggested.

The form of citations is: the author's surname followed by the date of publication e.g. (Szederkényi, 1996). In case of two authors: (Rosso and Bodnar, 1995) If there are more than two authors, after the first name the co-authors must be denoted as "et al.", e.g. (Roser et al., 1980).

### References

The reference list can only consist of published papers, M.Sc., Ph.D. and D.Sc. theses, and papers in press.

Only works cited previously in the text can be put in the reference list. Examples:

Best, M.G., Christiansen, E.H. (eds.) (2001): Igneous petrology. Blackwell, Edinburgh, 458p.

Upton, B.G.J., Emeleus, C.H. (1987): Mid-Proterozoic alkaline magmatism in southern Greenland: the Gardar province. In: Fitton, J.G., Upton, B.G.J. (eds.): Alkaline Igneous Rocks. Blackwell, Edinburgh, 449–472.

Rosso, K.M., Bodnar, R.J. (1995): Microthermometric and Raman spectroscopic detection limits of $CO_2$ in fluid inclusions and the Raman spectroscopic characterization of $CO_2$. Geochimica et Cosmochimica Acta, **59**, 3961-3975.

Szederkényi, T. (1996): Metamorphic formations and their correlation in the Hungarian part of Tisia Megaunit (Tisia Megaunit Terrane). Acta Mineralogica-Petrographica, **37**, 143-160.

Bakker, R.J. (2002): http://www.unileoben.ac.at/~buero62/minpet/Ronald/Programs/Computer.html. Accessed: June 15, 2003.

The full titles of journals ought to be given. In case more works of the same author are published in the same year, then these has to be differentiated by using a, b, etc. after the date.

### Illustrations

Finally, each figure, map, photograph, drawing, table has to be attached in three copies, they must be numbered and carry the name of the author on their reverse. All the illustrations ought to be printed on separate sheets, captions as well if possible. Foldout tables and maps are not accepted. In case an illustration is not presented in digital form then one of the copies has to be submitted as glossy photographic print suitable for direct reproduction. Photographs must be clear and sharp. The other two copies of the illustrations can be quality reproductions. Coloured figure, map or photograph can only be published at the expense of the author(s).

The width of the illustrations can be 56, 87, 118, or 180 mm. The maximum height is 240 mm (with caption).

All figures, maps, photographs and tables are placed in the text, hence, it is favourable if in case of whole page illustrations enough space is left on the bottom for inserting captions. In the final form the size of the fonts on the illustrations must be at least 1,5 mm, their outline must be 0,1 mm wide. Digital documents should be submitted in JPG-format. The resolution of line-drawings must be 400 dpi, while that of photographs must be 600 dpi. The use of Corel Draw for preparing figures is highly appreciated, and in this case please submit the .CDR file, as well.

### Proofs and offprints

After revision the author(s) receive only the page-proof. The accepted and revised manuscripts need to be returned to the Editors either on disc, CD or as an e-mail attachment. Proofreading must be limited to the correction of typographical errors. If an illustration cannot be presented in digital form, it must be submitted as a high quality camera-ready print.

The author(s) will receive 25 free offprints. On payment of the full price, further offprints can be ordered when the corrected proofs are sent back.

**Manuscripts for publication in the AMP should be submitted to:**

Dr. Pál-Molnár Elemér
E-mail: palm@geo.u-szeged.hu
Dr. Batki Anikó
E-mail: batki@geo.u-szeged.hu
Phone: 00-36-62-544-683, Fax: 00-36-62-426-479
Department of Mineralogy, Geochemistry and Petrology University of Szeged
P.O. Box 651
H-6701 Szeged, Hungary

Distributed by the Department of Mineralogy, Geochemistry and Petrology, University of Szeged, Szeged, Hungary.

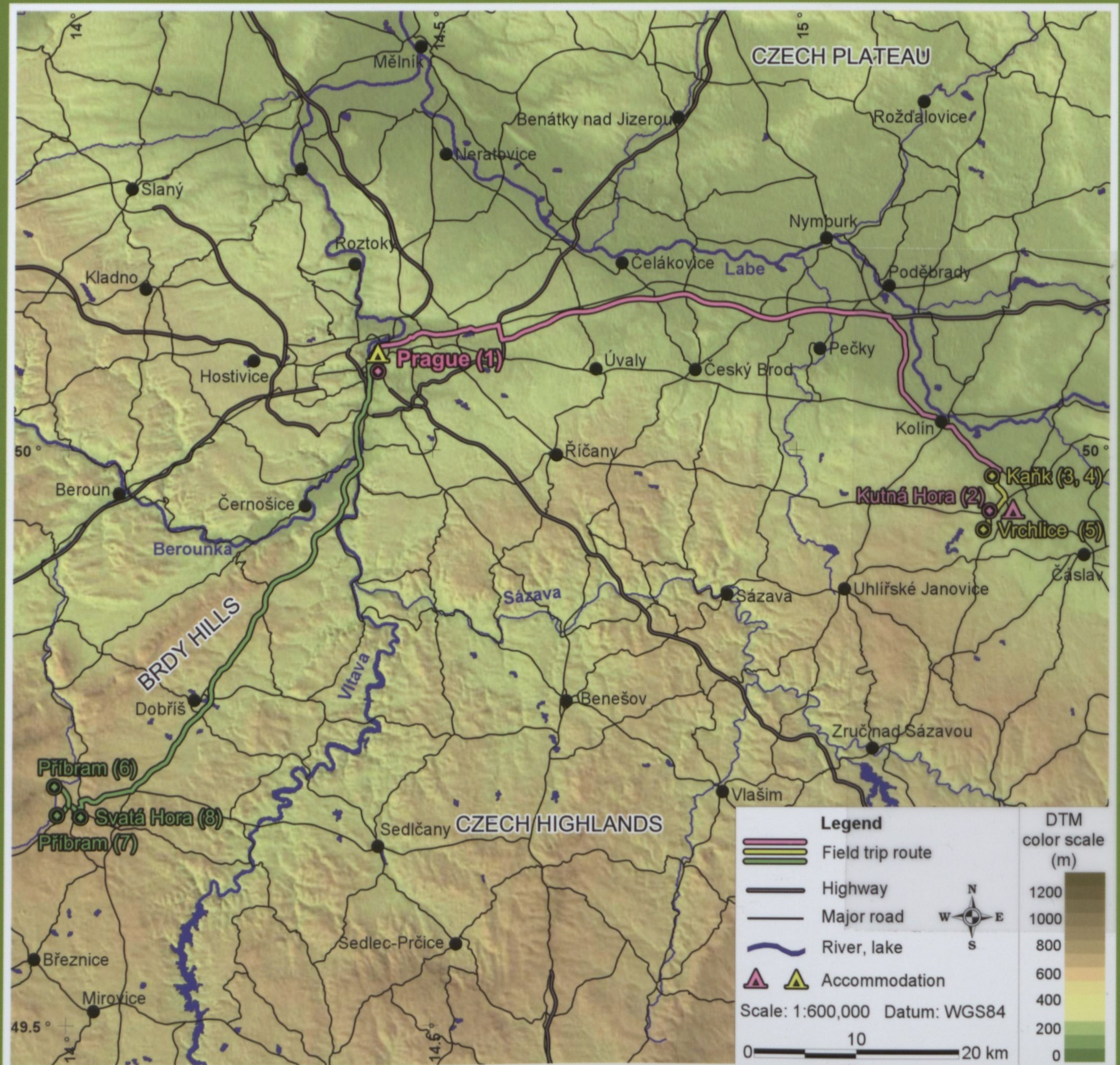
established in 1922

ACTA MINERALOGICA-PETROGRAPHICA
FIELD GUIDE SERIES

VOLUME 7 2010

HU ISSN 0324-6523
HU ISSN 2061-9766

MAP OF THE IMA2010 FIELD TRIP CZ3




Map provided by the Stockwork Exploration Ltd. (www.stockwork.eu)

Printed in Hungary by mondAt Ltd.